NITROSYL COMPLEXES
OF
MONOVALENT CHROMIUM

THESIS SUBMITTED FOR THE DEGREE OF

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by

Ram Charitra Maurya, M. Sc.

CHEMICAL LABORATORIES
Atarra Post Graduate College, Atarra (BANDA)
(U. P.), INDIA
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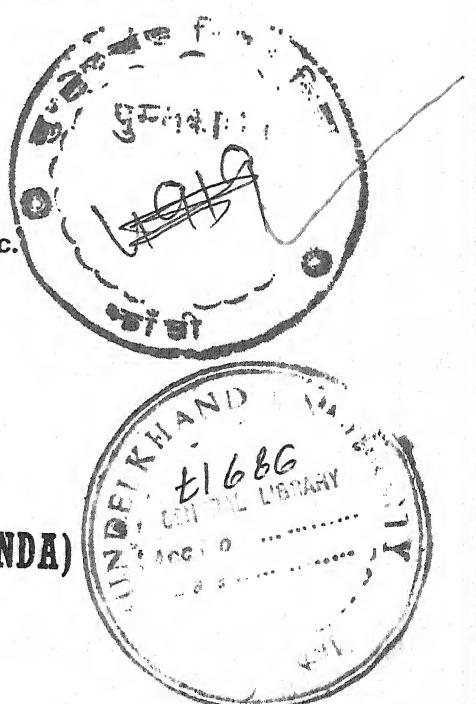
CERTIFICATE

This is to certify that the work embodied in the thesis entitled, "NITROSYL COMPLEXES OF MONOVALENT CHROMIUM" has been carried out by Sri Ram Charitra Maurya, Department of Chemistry, Atarra P.G.College, Atarra(Banda) under my supervision. He has full filled the requirements for the degree of Doctor of Philosphy in Chemistry of the Bundelkhand University, Jhansi regarding the nature and prescribed period of investigational work. The work reported in this thesis embodies the work of candidate himself.

(Dr.Raj Kishor Shukla)
Thesis Supervisor,
Head, Department of Chemistry,
Atarra P.G. College,Atarra(Banda),
U.P.(INDIA).

Dedicated to my revered father,

Shri Purusottam Maurya,

who has always been

a source of

inspiration

to me.

*

PREFACE

The investigation on the chemistry of chromium embodied in this thesis has been carried out in the Inorganic Chemistry Laboratories, T.D.College, Jaunpur and in Chemical Laboratories Atarra Post Graduate College,Atarra (BANDA).

The inception of nitrosyl Chemistry starts with the isolation of nitroprusside in 1849. But the knowledge of nitrosyl chemistry of chromium in monovalent oxidation state is very meagre uptil now and the present study involves the chemistry of nitrosyl complexes of chromium in this oxidation state. New series of complex compounds of monovalent chromium have been prepared and described in this thesis including penta-and hexacoordinated nonelectrolyte species using cyanide, thiocyanate, diethyldithiocarbamate, acetylacetone and a few mono and bidentate ligands, some of which are quite novel containing cyano bridging. Structural aspects of some of the representative type of complexes have been undertaken with the help of magnetic, infrared, electronic, electron spin resonance, x-ray photoelectron and mass spectral studies.

The reference cited in this thesis are covered upto the year 1978 and the part of the work presented in this thesis has been published in some Journals of Chemistry.

I wish to express my deep sense of gratitude to Professor R.P.Rastogi,Ph.D.,F.N.A.,Head of the Department of Chemistry,Gorakhpur University and Dr.S.Sarkar,Lecturer in Chemistry Department,I.I.T.,Kanpur for suggesting the

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Jan.,1981.

Chemical Laboratories,   (Ram Charitra Gaurya)

Atarra P.G.College,Atarra,

(Banda).

CONTENTS

GLOSSARY OF SYMBOLS

A$^{\circ}$	...	Angstrom Unit, 10^{-8} cm
acac	...	acetylacetonate
diars	...	o-phenylenebisdimethylarsine
dipy	...	2,2' dipyridyl
DTC	...	diethyldithiocarbamate
en	...	ethylenediamine
Et	...	ethyl
e.s.r.	...	electron spin resonance
eV	...	electron volt
I.R.	...	Infrared
L	...	ligand
Me	...	methyl
MO	...	Molecular orbital
NCS	...	thiocyanate
o-phen	...	ortho-phenanthroline
Ph	...	Phenyl
py	...	pyridine
PPh$_3$	...	triphenyl phosphine
Qu	...	quinoline
XPS	...	X-ray photoelectron spectroscopy
ν	...	stretching frequency, cm^{-1}
nm	...	nanometer, 10^{-9}m = 10A$^{\circ}$
δ	...	bending frequency, cm^{-1}
ϵ	...	molar extinction coefficient

| μ_{eff} | ... | effective magnetic moment in B.M. |
χ	...	magnetic susceptibility
β	...	beta
γ	...	gama
Λ_M	...	molar conductance

Chapter I

This chapter describes a brief and general account
of the cyanonitrosyl complexes of transition metals
followed by their bonding nature and structural aspects.
As an out come of these, the scope of the present work
has also been stressed in this chapter.

A-INTRODUCTION

Transition metal complexes containing nitric oxide as a coordinating ligand have been known by for over a century.[1] In this field, experiment has, in the main, out run theory. This is so because NO is treated as a good ligand comparable to CO, yet the main differences between these two ligands are:

(1) a wide variety of reagents can be employed as a source for nitrosylation whereas in carbonyl complexes, it is dominated by using CO as the source for carbonylation in varied temperatures and pressures.

(2) The apparent lack of reactivity of nitrosyl complexes compared to the carbonyl complexes. The development of new approaches in synthesizing nitrosyl complexes stemmed from the usefulness of nitrosylation using NO with high pressure high temperature technique due to its thermodynamic instability and its tendency to function as an oxidising agent.

$$3 \text{ NO} \longrightarrow N_2O + NO_2 \qquad H = -37.2 \text{ kcal mol}^{-1} \qquad .. (1)$$

$$NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2 \qquad H = -21.6 \text{ kcal mol}^{-1} \qquad .. (2)$$
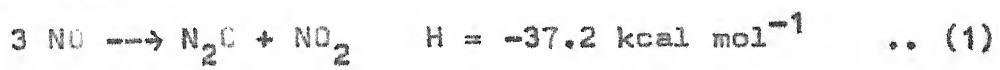
The mode of bonding of coordinated NO and CO have long been considered as analogous and in that sense CO, CN^-, NO^+ and N_2 as isoelectronic ligand, coordinate in a similar manner because they have same external electronic configuration. The bonding in nitrosyl complexes in the

simplest form is assumed as an electron transfer from NO to the metal proceeds the coordination of NO^+ through the nitrogen lone pair. π-back donation from the metal to the $\overset{*}{\pi}$ antibonding orbital of the NO^* reinforces the lone electron pair donation of nitrogen. In this sense NO functions as a three electrons donor compare to other isoelectronic ligands which are formally two electrons donor.[2-4] In this type of mode of bonding several attempts were made to interpret the wide region of 1950-1100 cm^{-1} nitrosyls stretching in infrared spectral studies. To cover the lowest range of $\nu(NO)$ for the red isomer of $[Co(NH_3)_5NO]^{2+}$, it was argued that there was a transfer of an electron from the metal to NO, the NO^- then acting as a normal ligand with donation of two electrons to the metal[5]. However, the red isomer of $[Co(NH_3)_5NO]^{2+}$ was latter found to have a quite different structure which is a dimeric cation $\{[Co(NH_3)_5]_2(N_2O_2)\}^{4+}$, where the hyponitrite ion is asymmetrically bonded to the two cobalt moiety in a trans arrangement[6].

The long search for NO^- complex predicted as early as 1934 by Sidgwick[1(a)] culminated in the complex $[Ir(Cl)(CO)(NO)(PPh_3)_2]BF_4$. In this case NO^+ is believed to be coordinated as a Lewis acid accepting an electron pair from the week base iridium(I). In other

words the coordinated nitrosyl group can be treated as NO^- in the formal oxidation state of iridium as +3. In other words two canonical forms may be depicted as follows:
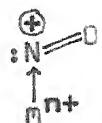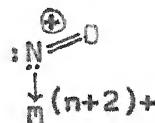
(a)   (b)

Thus it is generally assumed that in the bent form of coordinated NO, it functions as a one electron donor.

Besides these two extreme formulations of terminal bonding of nitrosyl group, in a few cases it can acts as a doubly bridging group, for example $(h^5-C_5H_5)(NO)Cr(\mu-NO)(\mu-NH_2)Cr(NO)(h^5-C_5H_5)$[7]. NO can acts even as triply bridging group as has been observed in the complex $(h^5-C_5H_5)_3Mn_3(NO)_4$[8].

Cyanonitrosyl complexes have drawn a distinction from other metal nitrosyls, although they are not basically different from other nitrosyl complexes. Among these $[M(CN)_5NO]^{n-}$ species have received special attention. A survey on the existing literatures suggest the formation of these species from different transition metals as shown in Table -1.

Table-1

V	Cr	Mn	Fe
X	Mo	X	Ru
X	X	Re	Os

In other stereochemistry, nickel forms $[NiNO(CN)_3]^{2-}$ as tetrahedral geometry[9] and vanadium gives, $K_4[VNO(CN)_6]$ as pentagonal bipyramidal geometry.[10,11]

The cyanonitrosyl complexes were synthesized using typically different methods. Each method is suitable for a particular transition metal as summarised below:

(i) <u>The action of nitric acid on a cyano complex of a transition metal</u>:

This method has been first employed for the preparation of sodium pentacyanonitrosylferrate, commonly called sodium nitroprusside by the reaction of nitric acid on sodium hexacyanoferrate.[12] The same method has been used for the preparation of analogous ruthenium and osmium complexes.[13] Treatment of $Na_3[Re(CN)_5(H_2O)]$ with moderately strong nitric acid is said to yield $Na_2[Re(CN)_5NO]$[14]. A diamagnetic nitrosylcyano complex of suggested composition $Ag_3[Re(CN)_7(NO)]$, obtained (contaminated with AgCN), when $K_3[Re(CN)_8]$ is warmed with 2 molar nitric acid.[15]

(ii) <u>The reaction of nitric oxide on a cyano complex of</u>

A <u>a transition metal</u>:

Nitric oxide reacts with $K_4[Ni_2(CN)_6]$ in liquid ammonia suspension to form deep violet $K_2[Ni(CN)_3(NO)]$.[16]

(iii) <u>Alkaline hydroxylamine method</u>:

Hieber and coworkers first exploited the use of hydroxylaminehydrogenchloride as a nitrosylating agent[17] tracing back an observation made by Vonder Heid and Hofmann.[18] The reaction of MoO_3, KOH and hydroxylamine-hydrogenchloride in aqueous medium gives a violet product of composition, $K_4[Mo(NO)(CN)_5] \cdot 2H_2O$.[17] There was some controversy to formulate this compound and an alternate octacoordinated structure $K_4[Mo(OH)_2(CN)_5]$ was proposed by Griffith, Lewis and Wilkinson.[19] X-ray studies finally confirm the hexacoordinated structure and composition of the compound is really $K_4[Mo(NO)(CN)_5] \cdot 2H_2O$.[20] Wilkinson and coworkers then utilized this procedure on other oxometallate anions. Thus with CrO_4^{2-}, the green complex $K_3[CrNO(CN)_5] \cdot H_2O$ was isolated.[19] Similarly using the same procedure with VO_3^-, an orange coloured complex of composition, $K_5[VNO(CN)_5] \cdot 2H_2O$ was isolated[21] which was structurally characterized as $K_3[VNO(CN)_5] \cdot 2H_2O$ by X-ray crystallography.[22] Interestingly using a slight different procedure that is a VO_3^- and hydroxylamine method, passes of H_2S leads to the isolation of yellow

coloured complex $K_4[VNO(CN)_6] \cdot {}^{10}H_2O$. It is interesting to know that for other oxometallates this method remains unsuccessful.

(iv) <u>Preparation using redox reactions</u>:

It is noteworthy to mention that the use of nitric acid as nitrosylating agent has been successfully applied to the synthesis of nitroprusside and its ruthenium and osmium analoges in the same formal oxidation states. Though oxidation state of the central metal attached with NO has got no sense in the real sense of the term, yet a formalism containing $(MNO)^{n+}$ would avoid an extreme formalism of NO either as NO^+ or NO^- (vide infra). In this sense by following the same process of preparation, Fe, Ru and Os give $(MNO)^{3+}$ moiety in their complexes. Contrary to this using hydroxylamine method of preparation chromium gives $(CrNO)^{2+}$ group whereas molybdenum gives $(MoNO)^+$ moiety. This prompted Griffith[23] to reduce the $(CrNO)^{2+}$ group containing compound, $K_3[CrNO(CN)_5] \cdot H_2O$ using polarographic method of reduction to isolate a blue reduced species $K_4[CrNO(CN)_5] \cdot H_2O$ analogous to $K_4[MoNO(CN)_5]$. There has been several attempts to isolate the one electron oxidation product of $K_4[MoNO(CN)_5]$ to obtain $[MoNO(CN)_5]^{3-}$ anion analogous to $[CrNO(CN)_5]^{3-}$,[24,25] but the pure green product, $(PPh_4)_3[MoNO(CN)_5] \cdot 2H_2O$ was isolated only very recently using air as oxidising agent.[26] Similarly

the purple coloured complex $K_3[MnNO(CN)_5]$. $2H_2O$ on oxidation with bromine or nitric acid gives yellow $K_2[MnNO(CN)_5]$. $2H_2O$.[27] The reduction of sodium nitroprusside with sodium in liquid ammonia yields ochre-yellow compound $Na_3[FeNO(CN)_5]$. $2NH_3$ as an unstable solid.[28] The corresponding tetraethylammonium salt when treated with acetic acid in acetonitrile converts it into a blue coloured complex, $(Et_4N)_2[FeNO(CN)_4]$.[29]

B- THE STRUCTURAL CHEMISTRY OF NITROSYLCYANO COMPLEXES

Since the emphasis in this thesis is on the chemistry
of "Nitrosyl Complexes of Monovalent Chromium," which was
explore using some substitution reactions, it is proper
to discuss briefly different physico-chemical methods
employed so far for the elucidation of the structural
aspects of the starting complex along with the trends
observed with the alike complexes of the other transition
metals. The shapes of the complex ions are of great inter-
est which can account for an indication of the relative
strengths of chemical reactivities in these complexes(vide
infra). Therefore some general comments on results of
X-ray diffraction studies, magnetic measurement studies
along with e.s.r. spectra, redox properties, vibrational
spectra, electronic spectra and photoelectronic spectra
are reviewed here.

(i) X-ray Diffraction Studies:

The representative nitrosyl cyano complexes whose
structural analysis have been made are presented in
Table 2. Interestingly in all these complexes, the M-N-O
angle nearly approaching to 180° and hence the M-N-O
group attachment is linear. Among the hexacoordinated
complexes the shortest M-N distance is found for$(FeNO)^{3+}$
group and the largest has been encountered for$(CrNO)^{2+}$
group considering the first transitional series. The

<u>Table-2</u>

Compound	M-N (Å)	N-O (Å)	Reference
$K_3[VNO(CN)_5] \cdot 2H_2O$	1.66	1.29	22
$K_4[VNO(CN)_6] \cdot H_2O$	1.686	–	11
$K_3[CrNO(CN)_5] \cdot H_2O$	1.99	1.21	33
$[Co(en)_3][CrNO(CN)_5] \cdot 2H_2O$	1.71	1.21	30
$K_3[MnNO(CN)_5] \cdot 2H_2O$	1.66	1.21	31
$Na_2[FeNO(CN)_5] \cdot 2H_2O$	1.63	1.13	32
$(Et_4N)[FeNO(CN)_4]$	1.56	1.16	29
$K_4[MoNO(CN)_5]$	1.95	1.23	20
$(PPh_4)_3[MoNO(CN)_5] \cdot 2H_2O$	1.921	1.195	26

reported C-N distance for all these complexes is of constant value whereas for the N-O distance one can observe some variations. The expected trend is observed for the $(MoNO)^+$ and $(MoNO)^{2+}$ groups with respect to Mo-N and N-O bond distances. The insensitiveness of C-N bond distance is suggestive that stabilization of the metal is mainly done by the nitrosyl group. Quite expectedly vibrational spectroscopy can explain this trend along with the changes in N-O bond distance (vide infra). The pentacoordinated complex containing $(FeNO)^{2+}$ group has a tetragonal pyramidal structure. The short Fe-N distance is suggestive of strong trans directing effect of the coordinated nitrosyl group and by virtue of this effect, the compound was isolated at low pH.[29] The only known heptacoordinated complex is pentagonal bipyramid in nature and though the stability of this compound was sometimes thought unusual which can now be explained easily on the structural data in the bonding scheme (vide infra).

(ii) Magnetic Measurement Studies:

In advancement of bonding scheme of nitrosyl complexes (vide infra), the observed magnetic moment values are quite expected. Taking into account as metal and nitrosyl group together (because of the fact that nitric oxide is itself paramagnetic with

respect to one unpaired electron), the number of total electrons present in this group are given in Table 3 alongwith the expected number of unpaired electrons and the observed magnetic moment values. The strong covalent nature of M-NO bonding is now certain from the studies of other physico-chemical measurements and X-ray structural analysis. The bonding scheme presented in Fig. 1(b) shows the nature of this interaction and though cyanide group in most of its complexes behave as a good π-bonding ligand, in cyanonitrosyl complexes the strong interaction between metal ion and nitrosyl group is enough to cause the separation of bonding, nonbonding and antibonding orbitals to a large extent. In these hexacoordinated complexes maximum symmetry expected is C_{4v} leading to a strong tetragonal distortion. Thus the ordering of these orbitals according to Fig. 1(b) is $(2e) < (1b_2) < (3e)$. The bonding orbital below '2e' will accommodate the ligands electrons. Thus filling up of the 'd' electrons on the metal will start from '2e' level. Rationalization of the bonding scheme has been done mainly on the consideration that the nitrosyl ligand is formally considered as $N \equiv O^+$. This assumption is only to accommodate the nature of the π-bonding which is vital to the linear mode of NO coordination. From the valence bond picture, the
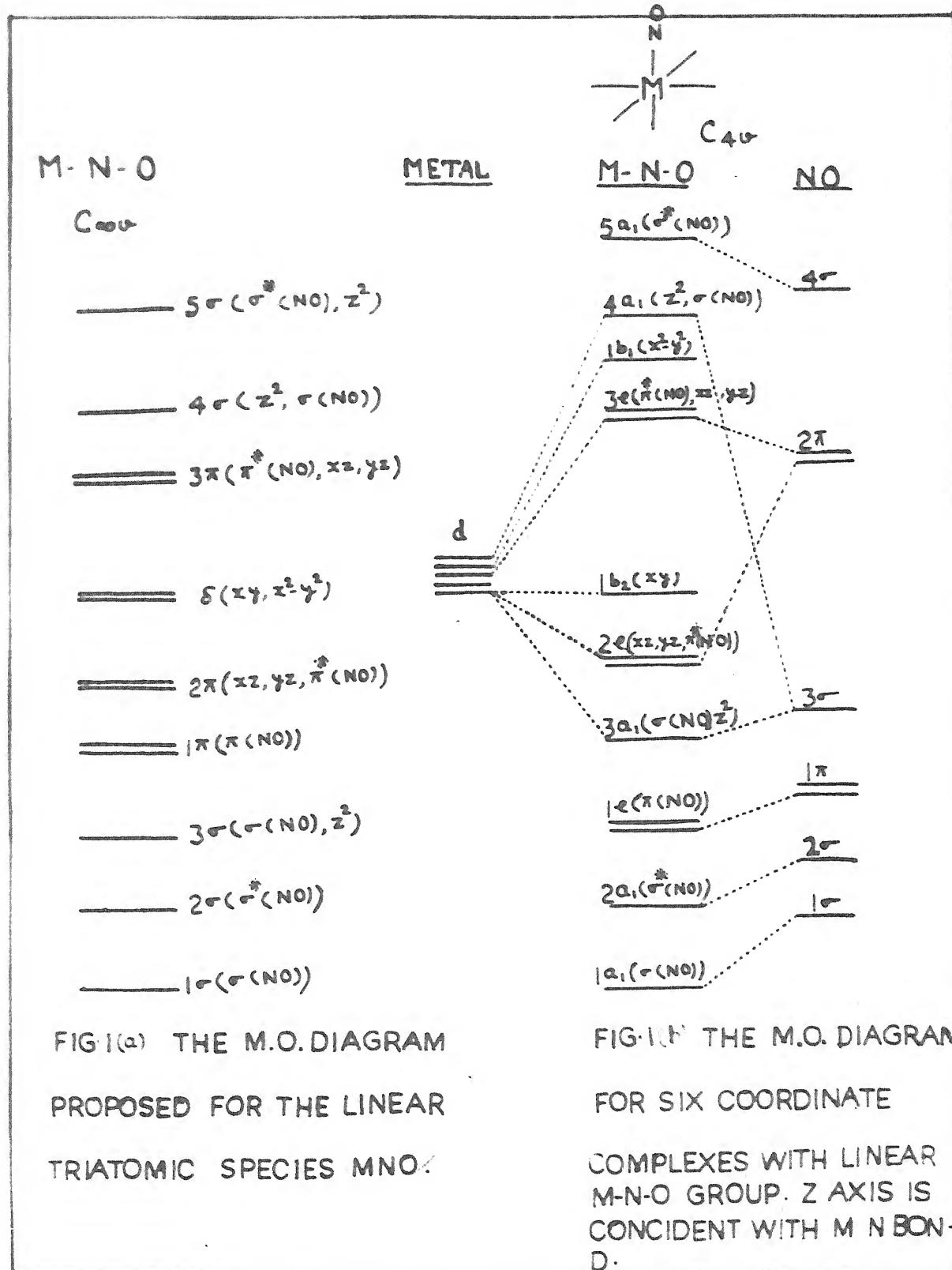
FIG·1(a) THE M.O. DIAGRAM PROPOSED FOR THE LINEAR TRIATOMIC SPECIES MNO.

FIG·1(b) THE M.O. DIAGRAM FOR SIX COORDINATE COMPLEXES WITH LINEAR M-N-O GROUP. Z AXIS IS CONCIDENT WITH M N BOND.

Table-3

Compound	Electron configuration $(MNO)^{n*}$	Expected number of unpaired electron	Expected mag.moment spin only value (BM)	Observed mag. moment (BM)	Ref.
$K_3[VNO(CN)_5] \cdot 2H_2O$	$\{VNO\}^4$	0	0	D	21
$K_4[VNO(CN)_6] \cdot H_2O$	$\{VNO\}^4$	0	0	D	10
$K_3[CrNO(CN)_5] \cdot H_2O$	$\{CrNO\}^5$	1	1.73	1.87	19
$K_4[CrNO(CN)_5] \cdot 2H_2O$	$\{CrNO\}^6$	0	0	D	23
$K_3[MnNO(CN)_5] \cdot 2H_2O$	$\{MnNO\}^6$	0	0	D	27
$K_2[MnNO(CN)_5] \cdot 2H_2O$	$\{MnNO\}^5$	1	1.73	1.73	27
$Na_2[FeNO(CN)_5] \cdot 2H_2O$	$\{FeNO\}^6$	0	0	D	27
$(Et_4N)[FeNO(CN)_4]$	$\{FeNO\}^7$	1	1.73	1.75	28
$K_4[MoNO(CN)_5]$	$\{MoNO\}^6$	0	0	D	17
$(PPh_4)_3[MoNO(CN)_5] \cdot 2H_2O$	$\{MoNO\}^5$	1	1.73	1.96	26

n^* = number of electrons in 'd' orbital; D= diamagnetic.

bonding of NO to transition metal ions can be treated by several possible ways which are shown below:

$$1 \leq n < 2$$
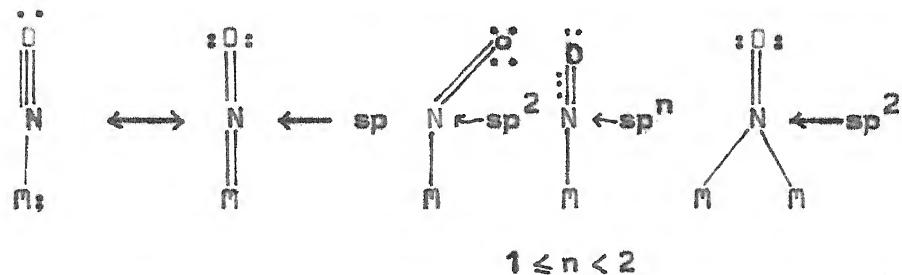
Linear I   Bent II   III   Bridging IV

Keeping this view in mind it is worth mentioning that the NO^+ formalism in general is merely an useful construct and the oxidation state formalism and the electron neutral approach are not intended as substitute for detailed bonding descriptions. In this regard keeping the metal nitrosyl component as an inseparable entity, $\{MNO\}^n$ (n = number of 'd' electrons present in the metal ion considering coordinated NO as NO^+) nomenclature is a practical approach.[51] In this formalism the cyanonitrosyl complexes may contain the electronic configuration $\{MNO\}^n$, where the value of n may be 4,5 or 6 which directly count the number of 'd' electrons. Obviously complexes containing n = 4 or 6 will show diamagnetism and for n=5 paramagnetism with respect to one unpaired electron is expected. The magnetic moment values are presented in Table 3.

For the complexes containing d^5 configuration, the

spinorbit coupling constant would contribute in the
measured magnetic moment value. The spin-orbit coup-
ling constants for Mo(I), Mn(II) and Cr(I) are -450,
-300 and -190 cm-1 respectively, which will affect
the magnetic moment values a bit greater than the
spin only value at room temperature.[57] The observed
results for the chromium and molybdenum complexes
described here follow this trend. However, for the
manganese complex the magnetic moment measurement of
$K_2[MnNO(CN)_5]$ in solution gives the value correspond-
ing to spin only formula. Interestingly the magnetic
moment value of its silver salt, measured in the solid
state gives a sub-normal magnetic moment value of 0.55
B.M.[27] only. The reason for this anomaly is difficult
to explain.

(iii) Infrared Spectroscopy:

Recent X-ray studies has described in Table 2
revealed the presence of linear M-NO group and thus
the coordinated NO group can be regarded as NO^+. Thus
infrared spectra of this series of complexes are widely
used to obtain the information about the nature of metal
to ligand bonding. Although much is known about the
nitroyel stretching frequency that is the nature of
ligand vibration, it is only recently that some efforts
are made to locate the associated ν(M-NO) and δ(M-N-O) modes.

Characterisation of these low frequency vibrations
would reflect more directly to the state of the metal-
ligand bonding. The first meaningful work on this aspect
is done by During and coworkers on the hexacoordinated
ruthenium nitrosylhalo complexes down to the frequency
of 50 cm^{-1}.[38] Contrary to the carbonyl compounds the
ν(M-NO) and δ(M-N-O) in general appear to low intensity
and thus possess additional problem. Furthermore, dealing
with the hydrated salts of cyanonitrosyl metallate, con-
siderable difficulties are encountered in localing
these vibrations because of the presence of librational
modes due to water and vibrations due to ν(M-CN) and
δ(M-C-N). Recently to avoid the complexity due to the
presence of water of crystallization, infrared studies
are made on unhydrous complexes Table 4. For the rela-
tive position between the metal-nitrogen stretching and
metal-nitrosyl deformation mode, assignments are made
from deducing the results obtained from the studies of
carbonyl and cyano complexes. In metal carbonyl complexes
ν(M-CO) is lower than δ(M-C-O). The same order is usually
obtained for complexed cyanides. However, unequivocal
assignment of these vibrations require ^{15}N and ^{13}C sub-
stitution data along with Raman polarization data. Some
of the work on ^{15}N substitution are done by Miki and
coworkers.[41] Using a linear three-body model, they assign

Table-4

Infrared spectral data of the cyanonitrosyl anions in the solid state (in cm^{-1}).

Compound	$\nu(CN)$	$\nu(NO)$	$\delta(M-N-O)$	$\nu(M-N)$	Ref.
$K_3[V(CN)_5NO].2H_2O$	2105, 2080	1530	–	–	22
$K_4[V(CN)_6NO].H_2O$	2095, 2100	1508	631	620	10
$K_3[Cr(CN)_5NO].H_2O$	2020, 2120	1630	612	621	35
$K_4[Cr(CN)_5NO].2H_2O$	2095, 2077	1470	627	645	35
$K_3[Mn(CN)_5NO].2H_2O$	2124, 2129	1706	660	660	36
$K_2[Mn(CH)_5NO]$	2150, 2100	1885	550	628	27,37
$Na_2[Fe(CN)_5NO]$	2144, –	1940	663	496	34
$(Et_4N)_2[Fe(CN)_4NO]$	2111, 2122	1755	–	–	29
$K_4[Mo(CN)_5NO]$	2120, 2106, 2097, 2080	1450	589	604, 595	35
$(PPh_4)_3[Mo(CN)_5NO]$	2040, 2023	1580	–	–	26

the higher wave number band to the M-N stretching vibra-
tion and to the lower one M-N-O bending vibration in the
lower frequency range. These assignments are definitely
more realistic than the assignments done on tentative
basis as presented in Table 4. The work of Miki and
coworkers on cyanonitrosyl metallates are summarized in
Table 5.

Taking representative example as ammine complexes,
ν(M-NH$_3$), a 'single bond'-stretching frequency appears
much lower[42] than those appeared for ν(M-NO) inspite of
the fact that the mass of the NO group is larger than
NH$_3$ group. This represents considerable π-backbonding
in nitrosyl complexes (vide infra).

(iv) Electronic Spectra:

Attempts to correlate the structural information
with a unified description of the bonding in metal
nitrosyl complexes formally remain not much of signi-
ficance. This is due to the fact that the inherent
question, still, lies on the fact that where nitrosyl
group is positive or negative which means how many 'd'
electrons are present in the compound ? Till date we
donot have any formal answer to this problem regarding
the formal oxidation state of the involved metal ion.
It is only in the first half of this decade that a
meaningful alternative description of the bonding in

Table-5.

Infrared spectra of pentacyanonitrosyl metallate(^{14}NO and ^{15}NO)complexes(cm^{-1})

Compound	^{14}NO complex			^{15}NO complex			Reference
	ν(NO)	ν(M-N)	δ(M-N-O)	ν(NO)	ν(M-N)	δ(M-N-O)	
K$_3$[Cr(CN)$_5$NO].H$_2$O	1643, 1635	620	610	1610, 1590	617	600	40
K$_3$[Mn(CN)$_5$NO]RH$_2$O	1741, 1733	663	663, 653	1704, 1694	660	651, 646	41
K$_3$[Mn(CN)$_5$NO].2D$_2$O	1736, 1728	663	663, 653	-	-	-	41
K$_3$[Mn(CN)$_5$NO]	1711, 1695	659	659	1675, 1663	661	648	41
Ag$_2$[Mn(CN)$_5$NO]	1888	628	628	1850	620	620	41

metal-nitrosyl complexes is developed. This is originated from the pioneering analysis of the structures of the triatomic species of the non-transition elements using the correlation method by Walsh,[45] which was first developed by Hund[46] and Mulliken[47] for diatomic molecule. Walsh's study is concerned with triatomic species which has only s and p orbitals in the valence shell of the atom and suggested that the concept should be generally applicable. Mingos and Ibers[48] have first applied this concept to understand the M-N-O angles in the metal nitrosyl complexes and Pierpont and Eisenberg[49] and Mingos[50] have utilized these concept in attempt to interprete the geometry of the tetragonal nitrosyl complexes. In a six coordinate complex of M-NO group, the maximum symmetry is C_{4v} and accordingly the modification of the molecular orbital diagram for the linear triatomic species MNO will change in $MNOL_5$ symmetry as shown in Fig. 1. In the molecular orbital diagram (Fig. 1b) the orbital $3a_1$ is primarily localised on the N-atom of the NO ligand and is σ-bonding with respect to MNO group. The degenerate $2e$ orbital is bonding with respect to M and N and antibonding between N and O. The $1b_2$ orbital is localised on the metal d_{xy} and is nonbonding. Thus an MNO complex with electronic configuration $(3a_1)^2(2e)^4$ has three bonding interactions between the metal and NO group which is similar to the

backbonding concept. The presence or absence of electron in the $1b_2$ orbital will affect very little in deciding the nature of bonding of the M-NO group.

It is experimentally difficult to know the ground state configuration of the diamagnetic complexes in this series. However, e.s.r. technique has been widely employed to investigate the ground state electronic configuration of paramagnetic complexes, especially $K_3[Cr(CN)_5NO]$. Though there is not complete agreement on the interpretation of the e.s.r. data of this complex made by several groups, yet the successful explanation of most of the e.s.r. parameters is consistent with the assignment of the 2_{B_2} ground state expected from the electronic configuration $(2e)^4(1b_2)^1$. Manoharan and Gray[43,44] using the information from the known crystal structure of $Na_2[Fe(CN)_5NO].2H_2O$ [32] assign the observed electronic transition of a series of cyanonitrosyl complexes. Though the agreement between the observed electronic transition energies and the calculated one electron energies is not very good, yet the model they have used can accommodate a wide variet of experimental facts is interesting. The obtained results of Manoharan and Gray are shown in Table 6.

Table-6

Electronic spectra of $[M(CN)_5NO]^{n-}$ in aqueous solution

Complex	Observed maxima (cm^{-1})	Max	Calculated energies (cm^{-1})	Band assignments	Ref.
$[V(CN)_5NO]^{5-}$	12,900	1.15	9,200	$^1A_1 \rightarrow {}^1E$ $(2b_2 \rightarrow 7e)$	
	21,160	36.5	19,000	$^1A_1 \rightarrow {}^1A_2$ $(2b_2 \rightarrow 3b_1)$	
	32,470	~1000	30,100	$^1A_1 \rightarrow {}^1A_1$ $(6e \rightarrow 7e)$	43
	37,470	~5200	23,260	$^1A_1 \rightarrow {}^1E$ $(2b_2 \rightarrow 8e)$	
$[Cr(CN)_5NO]^{3-}$	13,700	8	12,660	$^2B_2 \rightarrow {}^2E$ $(6e \rightarrow 2b_2)$	
	15,380	~1.5	13,890	$^2B_2 \rightarrow {}^2E$ $(2b_2 \rightarrow 7e)$	
	22,200	72	26,550	$^2B_2 \rightarrow {}^2B_2$ $(6e \rightarrow 7e)$	
	27,320	59	28,260	$^2B_2 \rightarrow {}^2B_1$ $(2b_2 \rightarrow 3b_1)$	43
	37,300	1100	37,420	$^2B_2 \rightarrow {}^2E$ $(5e \rightarrow 3b_2)$	
	43,480	3600	35,680	$^2B_2 \rightarrow {}^2E$ $(2b_2 \rightarrow 8e)$	

$[Mn(CN)_5NO]^{3-}$	18520	22.2	14,700	$^1A_1 \to {}^1E$ (2b$_2$ → 7e)	
	24,690	~60	24,200	$^1A_1 \to {}^1A_1$ (6e → 7e)	
	28,980	111.4	26,500	$^1A_1 \to {}^1A_2$ (2b$_2$ → 3b$_1$)	43
	37,850	~1000	37,770	$^1A_1 \to {}^1E$ (6e → 5a$_1$)	
	42,550	~4500	41,490	$^1A_1 \to {}^1E$ (6e → 3b$_1$)	
	45,450	~5000	40,470	$^1A_1 \to {}^1E$ (2b$_2$ → 8e)	

$[Mn(CN)_5NO]^{2-}$	12,050	19	7,820	$^2B_2 \to {}^2E$ (6e → 2b$_2$)	
	18,600	20	18,350	$^2B_2 \to {}^2E$ (2b$_2$ → 7e)	
	25,960	1700	26,170	$^2B_2 \to {}^2B_2$ (6e → 7e)	
	28,570	120	32,530	$^2B_2 \to {}^2B_1$ (2b$_2$ → 3b$_1$)	43
	32,280	880	28,830	$^2B_2 \to {}^2E$ (5e → 2b$_2$)	
	37,030	2400	38,740	$^2B_2 \to {}^2E$ (6e → 5a$_1$)	
	48,540	23800	45,050	$^2B_2 \to {}^2E$ (2b$_2$ → 8e)	

$[Fe(CN)_5NO]^{2-}$	20,080	8	20,540	$^1A_1 \to {}^1E$ (2b$_2$ → 7e)	
	25,380	25	25,090	$^1A_1 \to {}^1A_1$ (6e → 7e)	
	30,300	40	30,770	$^1A_1 -- {}^1A_2$ (2b$_2$ -- 3b$_1$)	44
	37,800	900	37,750	$^1A_1 -- {}^1E$ (6e -- 5a$_1$)	
	42,000	700	37,750	$^1A_1 -- {}^1E$ (6e -- 3b$_1$)	
	50,000	24000	4,900	$^1A_1 -- {}^1E$ (2b$_1$ -- 8e)	

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* see reference 22.

(V) <u>X-ray Photoelectron Spectroscopy</u>:

The X-ray photoelectron spectra may be used for studying
the chemical bonds in the coordination compond owing to the
fact that the binding energy E_b of the inner shell electrons
depends upon the effective charge q. The binding energies of
electrons of the atoms in chemical compound are usually cha-
racterised by the changes (shifts $\triangle E$) of these energies in
the compound studied compared to the energies in the refere-
nce compound. Free atoms are often used as reference compo-
unds. Under these conditions a postive shift corresponds
to the positive effective charge of the atom in the compound
under study and the negative shift corresponds to the nega-
tive charge. Th e direct correlation of the atomic charge
and the shift is a simplified procedure.

The effective charge of the NO group has been discussed
for over two decades.[54] This anomaly in this field is due
to the fact that the actual electron density distribution
is rather far from both limiting descriptions, NO^+ and NO^-,
and the absence of the clear cut physical concept of the
oxidation state in this case may give rise to apparent
contradictions. The oxidation states of the metal atom for
the sign of the charge of the NO group are determined by
evaluating how close certain physico-chemical characteristic
of the nitrosyl compounds are to those of the above limiting
cases. These characteristics are sensitive to various aspect

of the electron density distribution so that the boundary between the NO^- and NO^+ cases depends on the characteristic considered and the problem concerns only the definition of the oxidation state concept rather than the measurement of a physically observed parameters. Thus the closest correspondence to the classical chemical concepts, for example, the oxidation state of a metal atom, may be obtained with such observable parameters which describe the extent to which the electron density is drawn away from an atom or a group.

The N_{1S} value for NO^+ in $NOClO_4$ is about 409 eV and 406 eV is for the neutral molecule. The extrapolation of the data for NO^+ and NO yields the range of N_{1S} value for NO^- in the vicinity of 402 eV.

Folkesson[52] started a systematic photoelectron spectral study for a series of a nitrosylcyano complexes. The results are tabulated in Table 7. The N_{1s} binding energies for the cyanide group in this series reflect the observation made by $\nu(CN)$ in infrared spectroscopy as discussed earlier. Interestingly most of the N_{1s} binding energy forthe nitrosyl group falls below 402 eV and hence can be treated containing the nitrosyl group NO^-. According to the arguments put before, the nitrosyl group in nitroprusside can be said to contain a formally positive charged N that is NO^+. However, these data are insufficient

in the sense that they do not say anything about the
binding energies of the metal electrons. A comparison
of a series of a particular metal in its complexes con-
taining different oxidation states having the same coor-
dination number would have been more useful in assessing
the charge distribution. Furthermore, the ESCA data of
a nitrosylcyanometallate ions in its consecutive reduced
or oxidised form, as in some cases it is formed, would
supplement the study. The first point of the above views
has been studied by Nefedov[55] where he compared the
$Fe_{2p\ 3/2}$ energies in $Na_2[Fe(CN)_5NO]$, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$.
These data are presented in Table 8. alongwith the data for
$Fe(h^5-C_5H_5)_2$. The trend in Fe $2p_{3/2}$ according to the above
table suggests that iron in nitroprusside is in highly
oxidised state compared to even that in $K_3[Fe(CN)_6]$ meaning
thereby the formal oxidation state of iron in nitroprusside
would be IV. Furthermore in the absolute sense the N_{1s}
binding energy for NO is even lower for the neutral NO
molecule suggesting that the coordinated nitric oxide even
in nitroprusside should be treated as NO^-.

Attempts have been made by Sarkar and Muller[26,53,56]
to observe the changes appeared in the two adjacent
reduced and oxidised species of nitrosyl complexes of
molybdenum. This has been done on the ground to observe
the changes occur in the $3d_{3/2}$ and $3d_{5/2}$ binding energies

Table-7.

ESCA data of some of the cyanonitrosyl complexes

Compound	Eb N_{1s}(NO) eV	Eb N_{1s}(CN) eV	Electron configuration $\{MNO\}^n$	Reference
$[V(CN)_5NO]^{3-}$	400.6	398.8	$\{VNO\}^4$	52
$[Cr(CN)_5NO]^{3-}$	401.4	399.0	$\{CrNO\}^5$	52
$[Mn(CN)_5NO]^{3-}$	401.6	398.3	$\{MnNO\}^6$	52
$[Mn(CN)_5NO]^{2-}$	402.1	398.3	$\{MnNO\}^5$	52
$[Fe(CN)_5NO]^{2-}$	403.9	398.7	$\{FeNO\}^6$	52
$[Mo(CN)_5NO]^{4-}$	401.1	398.8	$\{MoNO\}^6$	52
$[Mo(CN)_5NO]^{3-}$	400.1	398.8	$\{MoNO\}^5$	26,53

Table-8.

Binding energies (eV) of some iron complexes

Compound	Fe $2p_{3/2}$ (eV)	N_{1s}^{NC} (eV)	Ref.
$Fe(h^5-C_5H_5)_2$	708.0		55
$K_4[Fe(CN)_6]$	708.8		55
$K_3[Fe(CN)_6]$	710.3		55
$Fe[Fe(CN)_5NO]$	711.3	402.6	55
$Na_2[Fe(CN)_5NO]$	711.0	403.6	55

of molybdenum alongwith N_{1s} binding energy of coordinated NO. For a redox reaction $\{MoNO\}^n \xrightarrow{-e} \{MoNO\}^{(n-1)}$ (n = number of d electrons) the overall electronic distribution in (MoNO) moiety will change. The release of an electron may takes place (a) from the molybdenum ion, (b) from the nitrosyl ligand, (c) an inseparable withdrawal of an electron from both the centres that is from MNO group. From the crystallographic data of $K_4[MoNO(CN)_5]$ and $(PPh_4)[MoNO(CN)_5].2H_2O$ (vide Table 2), It is known that the Mo-N bond in the oxidised species $\{MoNO\}^5$ is shorter than that of the $\{MoNO\}^6$ group contain--ing compound. This shortening is due to a stronger MoNO attachment in the former species than the latter. The stronger attachment can only be visualised by the increase back-donation from Mo $\rightarrow$ NO, leading thereby accumulation of more electron density on NO. The observed trend presented in Table 6 justifies these arguments. It is interesting to note that there is overall no electronic change of the cyanide groups present as co-ligand in both the complexes.

(vi) Redox Properties:

The one electron reduction of $[CrNO(CN)_5]^{3-}$ was first demonstrated by Wilkinson and coworkers.[19] They used the Polarographic method of reduction and could not be able to isolate the oxidised product at

that time. Few years latter, Griffith using same method have been able to isolate $[CrNO(CN)_5]^{4-}$. Cotton and co-workers have isolated the oxidised product (one electron) of $[Mn(CN)_5NO]^{3-}$ using bromine or nitric acid as oxidizing agent.[27] The extrastability achieved by coordinated nitric oxide for a particular metal can be seen from the isoelectronic redox systemfor the manganese complex(Table-9).

Table-9.

Standard electrode potential

Couple	E_0 (V)	Reference
$[CrNO(CN)_5]^{3-}/[CrNO(CN)_5]^{4-}$	-1.146	58
$[Mn(CN)_6]^{4-}/[Mn(CN)_6]^{5-}$	-1.06	59
$[Mn(CN)_5NO]^{2-}/[Mn(CN)_5NO]^{3-}$	+0.597	60

The nitroprusside analogue of rhenium[61] shows reduction which is a reversible one as may be expressed:

$$[Re(CN)_5NO]^{2-} + e^- \rightleftharpoons [Re(CN)_5NO]^{3-}$$

Jakob and coworkers studied quantitatively one electron oxidation of $[Mo(CN)_5NO]^{4-}$ which is a reversible one.[62] However, several attempts to isolate the oxidised product failed and it is only recently $[Mo(CN)_5NO]^{3-}$ has been synthesized and charactrised.[26] A comparative study

of the electrochemistry of $[Fe(CN)_5NO]^{2-}$ at NO^+ itself
has been made.[63] The nitrosonium ion shows three redu-
ction waves and these have been interpreted as the
formation of NO in the first stage which then dimerized
and reduced to $N_2O_2^{2-}$ in the second prt of reduction.
The third phase corresponds to three electrons reduction
of NO into NH_2OH. The $[Fe(CN)_5NO]^{2-}$ anion first undergoes
reduction to $[Fe(CN)_5NO]^{3-}$ which undergoes either proto-
nation and reduction via second wave or formation of the
complex $[Fe(CN)_5(NH_2OH)]^{3-}$. Polarographic reduction of
nitroprusside yields $[Fe(CN)_4(NO)]^{2-}$ which has been
isolated by the used conventional chemical method.[29]
This isolation demands a reinterpretation of the earlier
electrochemical studies on nitroprusside anion.[64,65]

(vii) Electron Spin Resonance Studied:

Most of the work in this field is related with the
investigation of e.s.r. spectrum of $[Cr(CN)_5NO]^{3-}$. Several
groups[66-74] have tried to interpret spectrum but there
is not complete agreement on the interpretation of the
observed data. The important experimental results may
be summarised as, an outcome of these investigations,
follows: (a) the 'g'- and chromium hyperfine tensor
have axial symmetry, (b) the nitrogen hyperfine tensor
has slight deviation from axial symmetry which may be
comparable to the deviation observed for the CrNO group,

(c) the nitrogen hyperfine tensor is highly anisotropy and $g\| < g\bot$.

The e.s.r. parameters for other hexa-coordinated compl exes of the family $[Cr(NO)L_5]$ [75-83] are as expected and depend on the electronegativity of L. The 'g' value comes closer to free electron value when there is more delocalisation. This is also reflected in NO stretching frequency.

The acid hydrolysis of $[Cr(CN)_5NO]^{3-}$ has been followed by e.s.r. method[115] by which it can be shown that the successive replacement of cyanide groups by water takes place.

Some times e.s.r. spectroscopy can affirmly predict the stereochemistry of a complex. This has been exemplified by the study of the oxidised species, $[Mo(CN)_5NO]^{3-}$ which was not isolated at the time,[26] but the e.s.r. parameters obtained for the oxidised species in the host of $K_3[Co(CN)_6]$ supports the formation of parent d^6 diamagnetic complex as $[Mo(CN)_5NO]^{4-}$ rather than $[Mo(NO)(CN)_5(OH)_2]^{4-}$, which was latter varified by X-ray studies.

The e.s.r. studies on $[Mn(CN)_5NO]^{2-}$ has been studied in detail 84-87 because of the interest in the ordering of the energy level in the corresponding Cr(I) and Fe(I) complexes. There is controversy existed to attribute the spin density on the NO group, where one group believe

this due to spin-orbit coupling whereas the other group feels that the spin polarisation mechanism is most likely.

Surprisingly γ-radiation of the diatomic $K_3[Mn(CN)_5NO]$[86] produced the oxidised $[Mn(CN)_5NO]^{2-}$ species by simple electron addition whereas nitroprusside loses an electron on irradation.

C. REACTIVITY OF COORDINATED NITRIC OXIDE :

The study of the reactivity of the nitrosyl complexes compare to the carbonyls are scare. This is due to the fact the coordinated nitric oxide is very firmly bound with the metal and a ligand displacement reactions are not found so commonly as these happen readily with the carbonyls. Due to the enormous studies on the carbonyls having industrial significance, in recent years many facets concerning the reactivity of nitrosyl complexes have emerged. Two things are of prime importance in these studies. The first one is to deal with the environmental pollution caused by nitric oxide and the second one is the development of newer catalytic system of industrial applicability.

The reactivity of coordinated nitric oxide falls under the following catagories.

(a) <u>Nucleophilic Attack</u>:

This is the most widely known reactivity of nitrosyl complexes which can be classically exemplified by the following reaction:

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O \qquad ...(1)$$

$$NO^+ + OH^- \rightleftharpoons NO_2^- + H^+ \qquad ...(2)$$
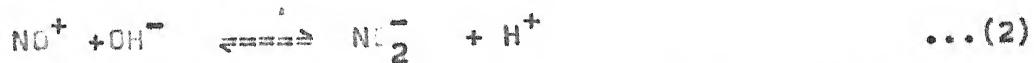
The equilibrium constants for the above two reactions are 1.5×10^6 and 2.3×10^{31} respectively which is suggestive

enough to infer that the coordinated NO^+ is a much weaker electrophile than free NO^+. The corresponding ruthenium and osmium analoges behave similarly.[88,89] A number of reactions are known where a lot of nucleophiles have been used instead of OH^- and the general reactivity is of the same nature as shown below:

$$PhNH_2 + NO^+ \longrightarrow PhNH_2^+ + H_2O \qquad\qquad\qquad (iii)$$

$$[Ru(Cl)(bipy)_2(NO)]^{2+} + PhNH_2 \dashrightarrow$$
$$[Ru(Cl)(bipy)_2(N_2Ph)]^{2+} + H_2O \;[90] \quad .. \quad (iv)$$

$$[Ru(NH_3)_5NO]^{3+} + NH_2OH \dashrightarrow [Ru(NH_3)_5N_2O]^{2+} + H_3O^+ \;[91] \;(v)$$
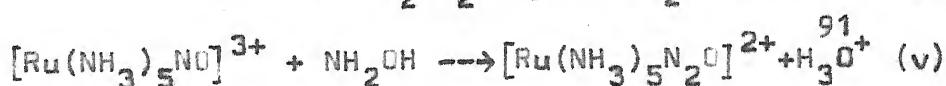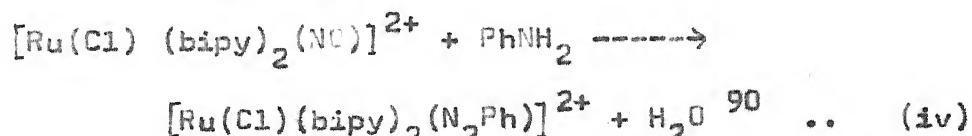
The formation of novel intermediate entities using this type of nucleophilic attack has been demonstrated by Bottomley and coworkers[92,93] which is shown below:

$$[Ru(NH_3)_5(NO)]^{3+} + OH^- \rightleftharpoons [Ru(NH_2)(NH_3)_4(NO)]^{2+} + H_2O$$

$$[Ru(NH_3)_5(NO)]^{3+} + [(Ru(NH_2)(NH_3)_4(NO)]^{2+} \dashrightarrow$$

$$\left([ON(NH_3)_4RuNH_2(O)NRu(NH_3)_5]^{5+}\right) \dashrightarrow cis\text{-}[RuOH(NH_3)_4NO]^{2+}$$
$$+ [Ru(NH_3)_5N_2]^{2+} + H^+ \quad .. \; (vi)$$
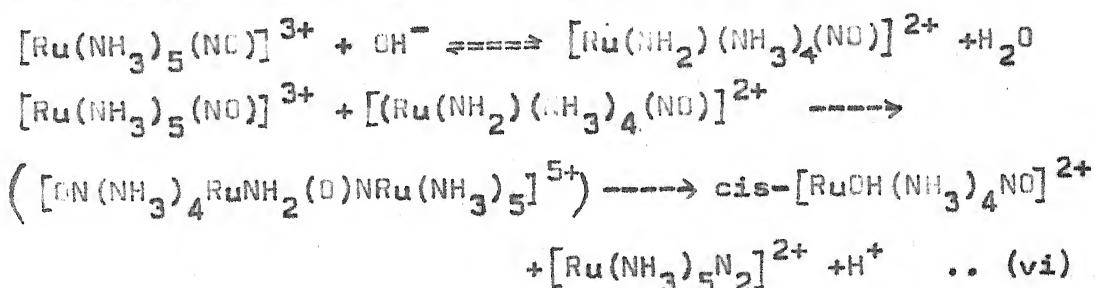
When N_3^- is used the reaction may be depicted as below:

$$[RuCl(dipy)_2NO]^{2+} + N_3^- \dashrightarrow [RuCl(dipy)_2S]^+ + N_2 + H_2O$$

where S indicates a solvent molecule.

The formation of the labile $[RuCl(dipy)_2S]^+$ has been synthetically exploited for preparation of $[RuCl(bipy)X]^{n+}$ complexes where X is a monodentate ligand.[94-98] In a

similar reaction with diarsine complex, the isotopic levell-
ing give evidence for attack of N_3^- at coordinated NO with
the formation of a cyclic N_4O intermediate as:

$$\left[RuCl(diars)_2NO\right]^{2+} + N_3^- \; -- \rightarrow \; \left[Cl(diars)_2Ru---N \; \overset{O}{\underset{N-----N}{\diagup \diagdown}} \; N \right]^+ \; \xrightarrow{\; N_3^- \;}$$

$$\left[Cl(diars)_2RuN_3\right] + N_2 + N_2O^{99}..(vii)$$
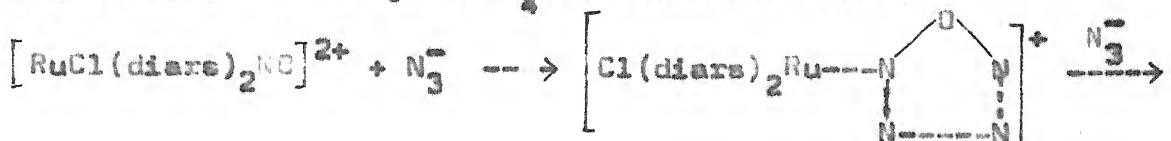
(b) Electrophilic Attack:

By the mode of attack it is evident that the activity
of the coordinated NO would be associated just in the oppo-
site direction as encountered earlier.

This attack is therefore associated with the nitrosyl
complexes where the M-N-O group is bent or in other words
the nitrosyl group contains formally NO^-. The extent of
protonation on this group depends on the formal oxidation
state of the metal and the trends observed are shown below:

$$Os(Cl)(CO)(NO)(Ph_3)_2 + HCl \rightarrow Os(Cl)_2(CO)(HNO)(Ph_3)_2(Os^I, d^7)$$
$$... (viii)$$

$$Os(NO)_2(Ph_3)_2 + 2HCl \longrightarrow Os(Cl)_2(NH_2H)(NO)(Ph_3)_2(Os^O, d^8)$$
$$... (ix)$$

$$Ir(NO)(Ph_3)_3 + 3HCl \rightarrow Ir(Cl)_3(NH_2OH)(Ph_3)_2(Ir^O, d^9) \quad 100$$
$$... (x)$$
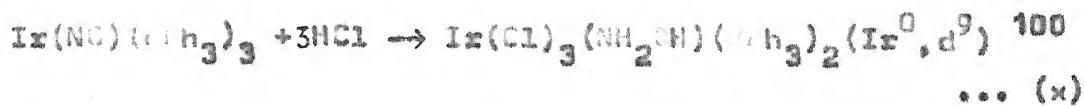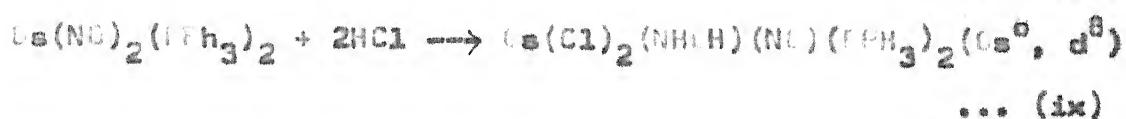
The above cited nucleophilic and electrophilic attacks
suggest a broad division like the linear M-N-O group conta-
ining NO^+ should be unstable in alkaline medium whereas the

bent M-N-O group containing NO⁻ would be unstable in acidic medium. From the synthetic point of view, the cyanonitrosyl complexes prepared in acidic medium (vide supra)should behave like nitroprusside anion and which is infact found to be true. Contrary to this, the cyanonitrosyls prepared using alkaline hydroxylamine method, though somewhat unstable in acidic medium, donot contain bent nitrosyl group (vide supra). Nevertheless, it has been demonstrated recently that complexes containing the same moiety can be isolated in alkaline and in acidic media as well.[26] This once more reflects our lack of understanding about the variation of actual electron density in the linear M-N-O group. Attempts are being made to answer this uncertainity,[101] however, a complete answer is still unknown.

(c) Reduction and Disproportionation:

As described earlier (vide supra) that one electron reduction of $[Fe(CN)_5NO]^{2-}$ gives brown $[(Fe(CN)_5NO]^{3-}$ which ultimately affords $[Fe(CN)_4NO]^{2-}$. The reduction of $\{Fe^{III}NO\}^6$ moiety has been explained to proceed to $\{Fe^{II}NO\}^7$ as intermediate in the brown complex which ultimately changes to $\{Fe^INO^+\}^7$.[102] The reduction can commonly occure at the metal centre[103] and there are some example where reduction takes place on the co-ligand sites.[104] In nonprotic media multielectron reduction of $[Fe(CN)_5NO]^{2-}$ gives $[Fe(CN)_5NO]^{3-}$, $[Fe(CN)_4NO]^{2-}$, $[Fe(CN)_4NO]^{3-}$, $[Fe(CN)_3NO]^{3-}$ and $[Fe(CN)_3NO]^{4-}$.

Using dispersed platinum metals oxide or metal gauze as catalyst, the reduction of NO to either ammonia or dinitrogen has been achieved. This heterogeneous reduction is used in treatment of automobile exhaust gas pollution.[106] Using some rhodium and iridium nitrosyl and carbonyl complexes mixtures of NO and CO may be disportionated into N_2O and CO_2.[107]

(d) Some Other Reactions of Interest:

It is long known that NO can be inserted into M-C bond. A representative example is[108]

$$ZnR_2 + 2\ NO \longrightarrow Zn\left(\begin{array}{c}O=N\\C-N-R\end{array}\right)_2 \qquad .. \ (xi)$$

other transition metals have been used similarly.[109]

Recently it has been demonstrated that though a coordinated nitrosyl remains intact, yet it can activate the metal centre so that dimethylformamide can be bonded to the metal as carbamido moiety.[110]

The use of dinitrosyl molybdenum derivatives have been made for the olefin metathesis reaction involving the intermolecular exchange of alkylidine units between alkene via cleavage of C=C bond as cocatalyst.[111,112]

A very useful synthetic procedure has been observed where coordinated NO may be transferred to the other metal,[113] for example,

$$\left[Co(NO)(DMGH)_2\right] + \left[FeCl_2(PPh_3)_2\right] \dashrightarrow \left[Fe(NO)_2(PPh_3)_2\right]$$

$$+ \text{ other Product}$$
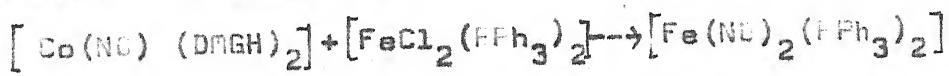
Ring strained olefin in the presence of NO gives dinitroso
product[114] as shown below:

$$[Co(h^5-C_5H_5)NO] \xrightarrow[\text{norbornene}]{NO} [Co(h^5-C_5H_5)(C_7H_{12}N_2O_2)] \quad \ldots \quad (xii)$$
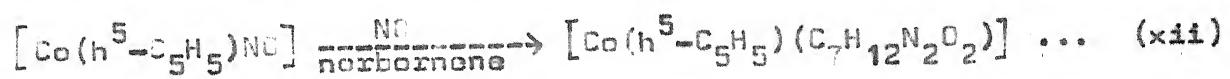
D. SCOPE OF THE WORK

The synthesis, bonding and reactivity of the nitrosyl complexes are complexed and varied. Mononitrosyl complexes containing $\{MNO\}^n$ group containing cyanide as coligand are comparatively less explored regarding substitution reactions keeping the (MNO) moiety intact. As described in the preceding part of the chapter, a fairly balanced physicochemical studies along with X-ray structural data are now available, but for accounting the reactivity of these complexes, there are definitely paucity of data compared to other nitrosyl derivatives. Among the cyannonitrosyl complexes it is only nitroprusside anion which received much attention in all respects.

The compariative rate of attention regarding substitution reaction in nitrosyl complexes containing cyano group as coligand as well as without cyano group are summarised in Table 10.

An examination of the table shows that except for d^6 configuration the cyanonitrosyl chemistry of other electronic configuration is very poorly studied with respect to their reactivity and substitution reactions. As a more general outlook, for the fast development of the nitrosyl chemistry containing electronic configuration d^6 and more lies on the theoretical interpretation regarding the electronic distribution in the MNO moiety. This is due

to the fact that on populating electrons in the antibonding orbital (vide supra) cause destabilization of the bonding between metal and nitrosyl centres enhancing thereby the reactivity of the coordinated NO group. Keeping these possibilities in mind different substitution reactions were carried out by changing the substituent coligand to get slight modification of the electronic distribution in the (MNO) group depending on the nature of σ-donor and π-acceptor capabilities of the substituent ligands. These manoeuvring some times lead to restrict the uncontrolable reactivity of the coordinated NO group or the reverse.

From the view point discussed above, it is obvious that the nitrosyl complexes containing d^6 electronic configuration do not feel any destabilization of that nature as the highest occupied orbital is nonbonding. However maximum studies on this electronic configuration were made on two grounds. Firstly from the theoretical consideration this electronic configuration can act some sort of a base line from which a comparison can be made for the others containing more number of d electrons. Secondly, it is of merely coincidental that nitrosyl complexes of this configuration already existed long back by the celebrated example of nitroprusside and easily recognized a class of nitrosyl ruthenium chemistry

before the bonding scheme are deviced resulting the
development of interpretative nitrosyl chemistry on
this electronic configuration.

The existing theories on different nitrosyl com-
plexes do not suggest anything of the d^4 and d^5 elect-
ronic configurations. This is partly responsible for the
paucity of nitrosyl complexes with these configurations
and when they are recently being explored, gave inter-
esting results. As it is often discussed earlier that
in cyanonitrosyl complexes stabilization rests mainly
on the nitrosyl group which indicates the cyanide coligand
should be mobile in nature and can be displaced by other
ligands of interest. A judicious choice of different
ligands containing different atoms at donor site would
be of much preparative interest and with their nature of
perturbation on the (MNO) moiety. One can think a bit
differently to see whether a particular condition, for
the introduction of nitrosyl group is very much specific
or not.

In the preparative sense, no substituted introysl
cyano complex of chromium (I) is reported. As acid hydro-
lysis of $[Cr(CN)_5NO]^{3-}$ [115] has been followed using e.s.r.
technique and also by polarography and optical spectroscopy,
it would be of interest to see whether the different
equation products can be isolated using nitrogen donors

like o-phen, dipy, Qu, py and picolines. This type of
nitrosyl derivatives are mostly known with the ruthen-
ium complexes containing d^6 configuration. As d^5 Cr(I)
and d^6 Ru(II) complexes contain the highest populated
orbital of nonbonding nature, a comparative chemistry
in light of bonding theories would be interesting.
Furthermore using other donor atoms containing ligand
like acetylacetone or dithiocarbamate, the relative
chemistry can be explored.

From Table 10, it is evident that complexes con-
taining $(CrNO)^{2+}$ moiety are mostly of the cationic type.
Anionic complexes is restricted to only on the prepara-
tion of $[CrNO(CN)_5]^{3-}$. It would be of interest to see
whether other anions of different complexing abilities
can be synthesized or not. The study of a series of
this type of species, if possible, would open a new
way to monitor their complexing abilities using e.s.r.
technique. A parallel chemistry of the recently repor-
ted $[CrNO(CNS)_5]^{3-}$ [26] thus can be made in detail. Besides,
nonelectrolytic type of complexes containing $(CrNO)^{2+}$
moiety is unknown. An attempt in this synthetic app-
roach would be interesting the scope.

The complexes thus synthesized would require an
attention of reactivity which can be dealt using diff-
erent physicochemical techniques already in existence.
Thus a correlation can be made on the changes noticed
with the help of existing theories in hand.

Table-10.

$\{MNO\}^n$ n = number of 'd' electrons	Coordination number	Relative chemistry with representative known species
d^4 With CN group	6 and 7	Poorly known $[VNO(CN)_5]^{3-}$, $[VNO(CN)_6]^{4-}$
Without CN group	5,6 and 7	Fairly known $[VNO(DTC)_2]$ $[MoNO(Cl)_5]^{2-}$ $[MoNOCl_4]^-$, $[MoNO(DTC)_3]$
d^5 With CN group	6	Poorly known $[CrNO(CN)_5]^{3-}$
Without CN group	6	Moderately known, containing $[CrNOL_5]^{2+}$
d^6 With CN group	6	Well known, $[FeNO(CN)_5]^{2-}$ and its derivatives
Without CN group	6	Well known, $[RuNOX_5]^{2-}$
d^7 With CN group	5 and 6	Poorly known, $[FeNO(CN)_4]^{2-}$ $[FeNO(CN)_5]^{3-}$
Without CN group	6	Moderately known, $[FeNOL_5]^{2+}$

---

d^8	With CN group	6	Poorly known, $[PtNO(CN)_5]^{2-}$
	Without CN group	5 and 6	Widely known, $[CoNO(NH_3)_5]^{2+}$ $[MnNO(CO)_4]$ $[Co(NO)L_2X_2]$, $[Mn(NO)_2L_2X]$

---

d^9	With CN group	—	Unknown
	Without CN group	4	Fairly known, $[Fe(NO)_2X_2]$, $[Co(NO)(L)(SR)]_2$

---

d^{10}	With CN group	4	Poorly known, $K_2[NiNO(CN)_3]$
	Without CN group	4	Most widely known, $[Mn(NO)_3L]$, $[Fe(NO)_2(CO)L]$, $[Fe(NO)_2L_2]$, $[Co(NO)(CO)_2L]$, $[Ni(NO)X]_n$, $[Ni(NO)L_2(X)]$, $[Fe(NO)_2(RNC)_2]$

Chapter II

This chapter describes the analysis of the
constituent elements and the procedures for
the preparation of complexes followed by
their properties.

EXPERIMENTAL

A- ANALYSIS OF THE CONSTITUENT ELEMENTS :

Nitrogen :-

When the compound contained thiocyanate group or ligands like o-phenanthroline, dipyridyl, etc., when a tertiary nitrogen was a member of the ring, the nitrogen content was determined microanalytically by Duma's method.

Carbon and Hydrogen :-

Carbon and hydrogen present in the sample were estimated microanalytically.

Estimation of Chromium :-

For the estimation of chromium as chromic oxide, the compounds were decomposed by heating with alkali followed by dissolving in nitric acid. Chromium was precipitated as chromic hydroxide by means of the slightest possible excess of dilute NH_4OH. The chromic hydroxide when ignited was converted into Cr_2O_3. Repeated heating, cooling and weighing were carried out until weight became constant.

Estimation of Sulphur :-

An aqueous suspension of the chromium complex containing sulphur was treated with bromine water and the solution was heated on a water bath for complete oxidation. Digestion was continued till the solution after evaporation of the excess bromine became perfectly colourless. The solution was then acidified with dilute HCl and the sulphate produced was precipitated by addition of $BaCl_2$ solution and estimated as usual.

B-PREPARATION AND PROPERTIES OF THE COMPLEXES :

Reagents :-

Reagents used for example, chromium trioxide, hydroxylaminehydrogenchloride, potassium hydroxide, potassium cyanide and ligands were of analytical grade. Deaerated water was used in all operations.

Preparation of potassium pentacyanonitrosylchromate(I)-hydrate, $K_3[CrNO(CN)_5].H_2O$:-

Potassium salt of pentacyanonitrosylchromate(I)monohydrate was prepared according to the procedure of Griffith, Lewis and wilkinson[19] and was characterised by elemental ana-lyses and infrared spectroscopy.

Found :

K, 33.8; Cr, 15.1; C,18.05; N, 24.2; H_2O,5.1%.

$K_3[CrNO(CN)_5]$ .H_2O requires K,33.8; Cr, 15.1 ;

C, 17.3; N, 24.2; H_2O, 5.2%.

B-1 Preparation of dicyanodipyridylnitrosylchromium(I), $[CrNO(CN)_2(dipy)]$:-

Into a filtered aqueous solution (20 ml.) of potassium salt of pentacyanonitrosylchroma-te(I)hydrate (1.5 g), a solution of dipyridyl (0.75 g) in acetic acid-water (1:1, 10 ml.) was added. The resulting solution was warmed for 10 min. and diluted with 30 ml. of water when a greenish yellow solid preci-pitated.The resulting mixture was freed from liberated

hydrocyanic acid by passing a current of CO_2 through the mixture for an hour and the precipitate was filtered off, washed with water, alcohol and ether and dried in vacuum to a constant weight and analysed. The yield based on pentacyanonitrosylchromate(I) was 80%.

Found :

        Cr, 18.1; N, 24.2; C, 49.6; H, 2.8%

        $[CrNO(CN)_2(dipy)]$ requires Cr, 17.9;

        N, 24.1; C, 49.7; H, 2.76%.

Preparation of dicyanoortho-phenanthrolinenitrosylchromium(I), $[CrNO(CN)_2(o-Phen)]$:-

                        A fittered aqueous solution (20 ml.) of potassium salt of pentacyanonitrosylchromate(I) hyrdrate (1.5 g) was added slowly into an aqueous-acetic acid (1:1, 10 ml.) of o-phenanthroline (1.0 g) with shaking when immediate greenish yellow solid started to precipitate. After the total addition, the liberated hydrocyanic acid was driven off in identical fashion as described earlier, and the precipitate was filtered off, washed with water, alcohol, ether and dried in vocuo.

Found :

        Cr, 16.7; N, 22.3; C, 53.5; H, 2.7%

        $[CrNO(CN)_2(o-phen)]$ requires Cr, 16.6;

        N, 22.3; C, 53.5; H, 2.5%.

Preparation of dicyanodi(pyridine)nitrosylchromium(I), $[CrNO(CN)_2(py)_2]$:-

A fittered aqueous solution (25 ml.) of potassium salt of pentacyanonitrosylchromate(I)hydrate (2.00 g) was added into an aqueous-acetic acid (1:1,15 ml.) of pyridine (2.5 ml.). The resulting green solution was immediately diluted with air free water (100 ml.)and the mixture was kept in warm condition. Carbondioxide was allowed to bubble through the solution to chase the liberated hydrocyanic acid when a yellow solid was started to precipitate. After two hrs. the precipitation was completed, which was filtered washed with water,alcohol and ether and dried in vacuo.

Found :

Cr, 17.8; N, 24.1; C, 48.9; H, 3.6%

$[CrNO(CN)_2(py)_2]$ requires Cr,17.8; N,24.0;

C, 49.3; H, 3.4%.

Preparation of dicyanobis(quinoline)nitrosylchromium(I), $[CrNO(CN)_2(Qu)_2]$:-

The complex was prepared by following an identical procedure described in the preparation of the corresponding pyridine complex just by replacing pyridine with quinoline and the passing of CO_2 was continued for a period of 6 hrs. to get the yellow coloured complex.

<u>Found</u> :

Cr, 13.1; N, 17.7; C, 61.0; H, 3.6%

$\left[CrNO(CN)_2(Qu)_2\right]$ requires Cr,13.3; N,17.9;

C, 61.2; H, 3.6%.

<u>Preparation of dicyanodi(β-picoline)nitrosylchromium(I)</u>,

$CrNO(CN)_2$ (β-picoline)$_2$:-

A somewhat identical procedure was followed as described earlier for the preparation of this complex replacing pyridine by β-picoline.

<u>Found</u> :

Cr, 16.2; C, 52.4; N, 21.8; H, 4.3%

$\left[CrNO(CN)_2\right.$ (β-picoline)$_2\left.\right]$ requires

Cr, 16.3; C,52.5; N, 21.9; H,4.4%.

<u>Preparation of dicyanodi(γ-picoline)nitrosylchromium(I)</u>,

$\left[CrNO(CN)_2(\text{γ-picoline})_2\right]$:-

This complex wasalso prepared by following an identical procedure described in the preparation of the corresponding pyridine complex just by replacing pyridine by γ-picoline.

<u>Found</u> :

Cr, 16.2; C, 52.3; N, 21.7; H, 4.3%

$\left[CrNO(CN)_2\right.$ (γ-picoline)$_2]$ requires Cr,16.3;

C, 52.5; N, 21.9; H, 4.4%.

<u>Properties of the cyano substituted complexes</u>,

$\left[CrNO(CN)_2 L_2\right]$:-

All the cyano substituted complexes are obtained as yellow highly dispersed solids having slight green tinge. They are exceptionally stable in

air and remain almost unattacked in dilute acids or alkalies and decomposed only on warning. Thermally they are also stable and do not show any melting or decomposition upto a temperature of 250°C (Table-11). All these complexes are slightly soluble in acetonitrile being insoluble in other common solvents. Ligands of good donor capacity like pyridine, dipyridyl or triphenylphosphine could not be accommodated in the sixth position even under drastic sealed tube reaction.

$[CrNO(CN)_2L_2]$ + excess py $\xrightarrow[\triangle]{sealed\ tube}$ no change.

$[CrNO(CN)_2L_2]$ + excess dipy $\xrightarrow[\triangle]{sealed\ tube}$ no change.

$[CrNO(CN)_2L_2]$ + excess pph$_3$ $\xrightarrow[\triangle]{sealed\ tube}$ no change.
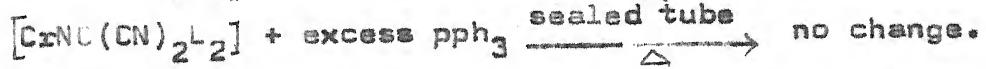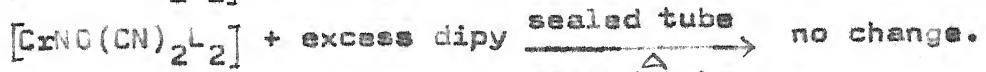
Attempts to methylate the cyano groups in the cyano substituted compounds using $(CH3)_2 SO_4$ or CH_3I in sealed tube were unsuccessful.

$[CrNO(CN)_2L_2]$ + CH_3I $\xrightarrow[\triangle]{Sealed\ tube}$ no change.

$[CrNO(CN)_2L_2]$ + $(CH_3)_2SO_4$ $\xrightarrow[\triangle]{Sealed\ tube}$ no change.
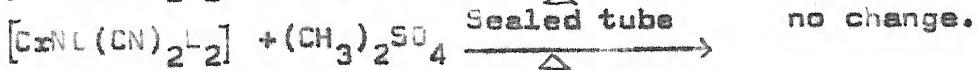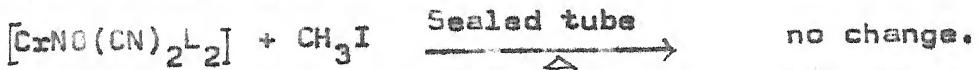
Methylation reaction was also found to be unsuccessful when it was carried out using CH_3I with HgI_2 in sealed tube. Though the products isolated in these reactions showed the presence of methylisocyanide retaining nitrosyl group yet they appeared to contain some decomposed product or unreacted starting compound.

$$[CrNO(CN)_2L_2] + CH_3I + HgI_2 \xrightarrow{\text{Sealed tube}} \text{partial}$$

<div align="right">decomposition
with no change.</div>
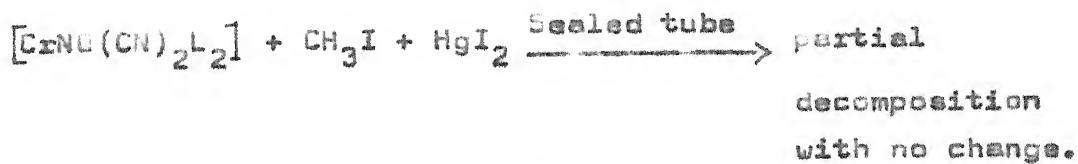
The molar conductance values of practically saturated anhydrous methanol solution (10^{-4}M) of these cyanonitrosyl complexes (Table-11) suggest their nonelectrolytic nature.

B-2 Preparation of bis(acetylacetonato)nitrosylchromium(I), $[CrNO(acac)_2]$:-

The complex was prepared by refluxing a mixture of $K_3[CrNO(CN)_5]$ (2.0 g) and excess acetylacetone (6 ml.) in an air tight compartment with an intermittent removal of the liberated Hydrocyanic acid by passing dry carbondioxide. After refluxing for 8 hrs., the excess acetylacetone was distilled off and the result ant mixture was cooled in vacuo over solid KOH. Traces of free acetylacetone were removed from the cooled brown mass by repeated washing with petroleum ether and brown crust was extracted with acetone. On evaporation of acetone, the solution gave brown crystals which were washed with petroleum ether. The crystallization process was repeated thrice. The crystals thus obtained were dried and analysed.

Found :

Cr, 18.6; N, 5.0; C, 42.9; H, 8.32%

$[CrNO(acac)_2]$ requires Cr, 18.6; N,5.0;

H, 8.23%.

Properties :-

      This nonelectrolytic monomeric complex (Table-11) is soluble in most of the common non-polar organic solvents but insoluble in water. Its stability is comparable to that of $Cr(acac)_3$ as it remains un-affected by concentrated alkalies or mineral acids in cold and decomposes only on prolonged boiling. This complex does not show any interaction with ethanol suggesting that solvation does not take place at the sixth position. But when it is refluxed with traces of pyridine in ethanol, pyridine shows interaction at the sixth position and this has been demonstrated by e.s.r. spectroscopy (vide infra).

B-3 Preparation of aquobis(diethyldithiocarbamato) nitrosyl romium(I), $[CrNO(DTC)_2(H_2O)]$:-

      1.0 g of potassiumpentacyanonitrosylchromate(I)dydrate was dissolved in 30 ml. of water and into it an aqueous solution of diethyldithiocarbomate (1.0 g) was added. Into the mixed solution 10 ml. of (1:1) dilute acetic acid was slowly added with stirring and the issuing gas was chased by a current of carbondioxide, whereby, reddish brown precipitate appeared which was filtered under suction, washed several times with water. This precepitate is now extracted with acetone and the red

—

brown compound was precipitated by adding petroleum
ether, washed with petroleum ether, dried and analy-
sed. The yield was appoximately 35%.

Found :

Cr, 13.2; C, 30.1; N, 10.5; H, 5.56%

$[CrNO(DTC)_2(H_2O)]$ requires Cr, 13.1; C, 30.3;

N, 10.6; H, 5.5%.

Properties :-

This complex is soluble in alcohol,
acetone and acetonitrile to impart orange red colour
and in methanol the complex is found to be non-elect-
rolytic in nature (Table-11).

B-4 Preparation of diisothiocyanatodipyridylnitrosyl-
chromium(I), $[CrNO(NCS)_2(dipy)]$:-

1.0 g of potassium-
chromate and 3.8 g of potassiumthiocyanate was taken
in a beaker and 40 ml. of water was added to dissolve
the mixture. 1.0 g hydroxylaminehydrogenchloride was
slowly added into the solution with stirring. A vigorous
reaction sets in and addition of hydroxylaminehydrogen-
chloride was cautiously done to control the temperature
(further addition leads to the expulsion of NO). After
the addition of hydroxylaminehydrogenchloride the
reaction mixture was stirred at room temperature for
an hr. and any grey colour precipitate was allowed to

Table-11

physical properties

Compound	Colour	Λ_M $\Omega^{-1}cm^2\ mole^{-1}$	m.p.	Mol.Wt.
$[CrNO(CN)_2(dipy)]$	Greenish yellow	10.2	$>250^{\circ}C$	
$[CrNO(CN)_2(o-phen)]$	Greenish yellow	13.5	$>250^{\circ}C$	
$[CrNO(CN)_2(py)_2]$	Yellow	15.2	$>250^{\circ}C$	
$[CrNO(CN)_2(Qu)_2]$	Brownish yellow	8.2	$>250^{\circ}C$	
$[CrNO(CN)_2(\beta-picoline)_2]$	Greenish yellow	13.2	$>250^{\circ}C$	
$[CrNO(CN)_2(\gamma-picoline)_2]$	Greenish yellow	14.3	$>250^{\circ}C$	
$[CrNO(acac)_2]$	Brown	13.2	$206^{\circ}C$	300
$[CrNO(DTC)_2(H_2O)]$	Reddish brown	17.3	-	

dissolve by adding dropwise dilute acetic acid. To the filtered green solution, 0.78 g of dipyridyl dissolved in dilute acetic acid was added, a khaki colour precipitate appeared which was stirred for an hr. at a temprerature around 90°C and filtered. The precipitate was washed several times with dilute acetic acid, finally washed with water, dried in air and recrystallised from methanol-petroleum ether. The yield was approximately 45%.

Found :

    Cr, 14.6; C,40.5; N, 19.7; H,2.1; S, 18.1%

    $[CrNO(NCS)_2(dipy)]$ requires Cr,14.7; C,40.7;

    N, 19.8; H,2.2; S, 18.0%.

Preparation of di*iso*thiocyanatoortho-phenanthroline-nitrosylchromium(I), $[CrNO(NCS)_2(o-phen)]$:-

                                   The corresponding o-phenanthroline complex was prepared analogously as described above just by replacing dipyridyl with o-phenanthroline. The olive green recrystallised compound was analysed.

Found :

    Cr, 13.6; C, 44.2; N, 18.3; H,2.1; S,16.8%

    $[CrNO(NCS)_2(o-phen)]$ requires Cr, 13.8;C,44.4;

    N, 18.5; H, 2.1; S, 16.9%.

<u>Preparation of diisothiocyantodipyridylpyridinenitrosyl-</u>
<u>chromium(I), [CrNO(NCS)$_2$ (dipy)(py)]</u> :-

About 0.5 g of
iso
di/thiocyanatodipyridylnitrosylchromium(I) was dissolved
in 15 ml. of acetone and 1 ml. of pyridine was added in-
to it. The soluti n was refluxed for about 2 hrs. on
water bath with positive pressure of the inside solvent
vapour (using a pool of mercury) and the resultant solu-
tion was vacuum concentrated. The product was isolated
from the solution by adding petroleum ether as yellow
solid which was recrystallised from acetonepetroleum
ether mixture. The yield was approximately 75%.
<u>Found</u> :

Cr, 11.9; C,47.0; N, 19.2; H, 2.9; S, 14.6%

[CrNO(NCS)$_2$(dipy)(py)] requires Cr,12.0;C,47.1;

N, 19.4; H, 3.0; S, 14.8%.

<u>Preparation of diisothiocyanatoortho-phenanthroline-</u>
<u>pyridinenitrosylchromium(I), [CrNO(NCS)$_2$(o-phen)(py)]</u> :-
The o-phenanthroline analogue of the previous compound
iso
was prepared analogously just by taking di/thiocyanato-
rtho-phenanthrolinenitrosylchromium(I) instead of
iso
di/thiocyanatodipyridylnitrosylchromium(I) as described
earlier. The yellow reprecipitated compound from ace-
tonep-petroleum ether mixture was dried and analysed.

Found :

Cr,11.3; C, 49.8; N, 18.2; H,2.7; S, 13.9%

$[CrNO(NCS)_2(o-phen)(py)]$ requires Cr,11.4;

C, 49.9; N,18.4; H, 2.8; S, 14.0%.

Properties of thiocyanato substituted complexes:-

The thiocyanato substituted complexes are greenish
yellow to yellow in colour and are highly soluble
in alcohol and acetone. Alcoholic or acetone solu-
tion of these complexes impart greenish yellow colour
and addition of methanolic silvernitrate does not give
any immediate precipitation but on standing silver is
deposited. The molar conductivity of $[CrNO(NCS)_2(dipy)]$
and $[CrNO(NCS)_2(o-phen)]$ are found to be 15.3 and 12.7
$\Omega^{-1}cm.^2$ $mole^{-1}$ respectively suggesting that the
complexes are nonelectrolytic in nature. The other
complexes are also nonelectrolytic in nature(Table-12).

It is interesting to note that complexes of
(CrNO) moiety with S- or O- donor are coloured reddish
brown whereas when the donor is only nitrogen the colour
is predominantly yellow. For mixed carbon-nitrogen donor
sites, colour is green.

All the complexes described here are somewhat
stable in acids but on treatment with alkali the com-
plexes decompose and the coordinated nitrosyl group
changes to NO_2^-, which can be tested by using Griess

Table-12.

Physical properties

Compound	Colour	Λ_M Ω^{-1} cm.^{2} mole^{-1}
$[CrNO(NCS)_2(dipy)]$	Khaki	15.3
$[CrNO(NCS)_2(o\text{-phen})]$	Olive green	12.7
$[CrNO(NCS)_2(dipy)(py)]$	Yellow	13.6
$[CrNO(NCS)_2(o\text{-phen})(py)]$	Yellow	12.9

reagent. This suggests that though the well known complex, $K_3\left[CrNO(CN)_5\right] \cdot H_2O$ has been isolated in strong alkali medium, yet depending on the nature of co-ligands the same $(CrNO)^{2+}$ moiety is attacked by alkali with the concomitant conversion of coordinated nitricoxide to NO_2^- as known for introprusside anion (vide-supra).

The physico-chemical aspects of these complexes have been discussed in the chapter of structural chemistry of the complexes.

Chapter III

This chapter describes the physico-chemical
investigations of the isolated complexes.
The studies include magnetic susceptibility,
infrared, electron spin resonance, mass,
x-ray photoelectron and electronic spectral
measurements.

STRUCTURAL CHEMISTRY OF THE COMPLEXES

A- General remarks :

The structural chemistry of the complexes synthesised during this investigation has been followed by magnetic measurements, infrered, electronic, electron spin resonance, X-Ray photoelectron and mass spectral studies.

The group $(CrO)^{2+}$ contains d^5 electronic configuration and thus this entity is of substantial importance for magnetic properties. Due to the strong tetragonal distortion of the complexes containing this group, e.s.r. measurement would be of great help in ascertaining the comparative complexing ability of the used π- bonding ligands as substituent and also would reflect a nature of charge distribution within $(CrNO)$ group.

Although, no detail magneto-chemical calculations regarding the bonding scheme of the prepared complexes containing $(CrNO)^{2+}$ moiety surrounded by different donor atoms is possible using the limited nature of measurements done here, yet an synthetic point of view the proper characterisation of the sites of coordination can be made with certainty.

The above mentioned conclusion can be amply supported by the other physico-chemical studies made in this investigation.

B-Experimental :

Conductance measurements :-

The conductivity was measured in analytical reagent grade methanol using a dip type cell with the help of philips conductivity bridge apparatus in the usual manner.

Magnetic susceptibility measurements :-

Gouy method was used for magnetic measurements. A magnetic field strength of 8500 gauss was employed. The apparatus was calibrated using cobalt mercury thiocyanate. $\chi'M$ (corrected molar magnetic susceptibility) values were obtained by using usual diamagnetic correction as given by Figgis and Lewis[116].

Infrared spectral measurements :-

These spectra were recorded over the range 4000 - 400 cm^{-1} using a Perkin Elmer infra-cord or Perkin Elmer- 621 or Perkin Elmer- 377 spectrometer. Spectra were taken in potassium bromide discs.

Electronic Spectral Measurements :-

The electronic and reflectance spectra were recorded in spec grade ethanol and nujol mulls respectively with the help of a carry - 14 spectrometer.

Electron spin resonance spectral measurements :-

e.s.r. measurements were carried out on either solutions or powdered samples. The parallel and

perpendicular components of the 'g' value were obtained
by measurement using potassium bromide as diluent.These
measurements were done using a varian- 4502 spectrometer
and DPPH was used as internal standard.

Mass spectral measurements :-

     Mass spectrum of $[(CrNO\ (acac)_2]$ was measured using
an Atlas -CH4 mass spectrometer. The complex is directly
introduced into the ion source and heated to a temperature
of $210^{\circ}C$.

X-ray photoelectron spectral measurements :-

     The photoelectronic spectrum for $[CrNO\ (acac)_2]$
was recorded using ESCA-3 type spectrometer of vacuum
generators. It is obtained using Al- Kα radiation
(1846.6 eV) at a pressure between 5×10^{-9}-1×10^{-8} torr.
The sample was mounted on gold planchettes. The binding
energy reported was standardised using a C(1s)binding
energy of 285.0 eV.

C-Results and Discussion :

  Magnetic measurements :-

     It has been well established that even in pentaaquo
complex containing the group $(CrNO)^{2+}$,that is,$[CrNO(H_2O)_5]^{2+}$
is paramagnetic with respect to one unpaired electron.The
ligands involved in the preparation of the complexes in
this investigation are mostly π - bonding type and thus
it is expected that these complexes should be of low

spin type containing only one unpaired electron. The
magnetic susceptibility values of the compounds described
earlier, have presented in Table-13. The magnetic suscep-
tibility values of the established complexes containing
this group are also included here for comparison. This
group are also included here for comparison. This
indicates paramagnetic range from 1.60 B.M. to 1.74 B.M.
for these complexes. The complexes of the type $[CrL_5NO]^{n\pm}$
containing $(CrNO)^{2+}$ group show magnetic moment values
slightly higher than the values obtained for these complexes.

An examination of the magnetic susceptibility values
of several known compounds (Table-13) shows a slightly
higher magnetic moment for one unpaired electron(1.73 B.M.)
from the spin only formula. This high moment has been
explained satisfactorily by Griffith and coworkers[19] to
show that this is due to spin and orbital interaction
in these complexes.

It is remarkable to point out that all the previ-
ously known compounds of this group are hexacoordinated
where as the cyanonitrosyl complexes described here are
all pentacoordinated. In the nitrogen donor ligands
irrespective of monodenate or bidentate or bulkiness
of the ligands, the complexes are highly insoluble in
common solvents suggesting polymeric nature. The magnetic
moment values of these complexes are significantly lower

Table-13

Magnetic properties

Compound	Physical state	Temp. °K	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	Diamagnetic correction $\times 10^{-6}$	$\chi'_M \times 10^{-6}$	μ_{eff} in B.M.	Ref.
$K_3[CrNO(CN)_5].H_2O$	Solid	297	-	-	-	-	1.87	19,23
$[CrNO(NH_3)_5][Cl_2.H_2O_2]$	Solid	295	-	-	-	-	2.3	23
$[CrNO(H_2O)_5](ClO_4)_2$	aqueous solution	295	-	-	-	-	2.2	23
$[CrNO(CN)_2(o-phen)]$	Solid	303	3.14	985.96	164.00	1149.96	1.67	
$[CrNO(CN)_2(dipy)]$	"	"	3.13	907.70	141.00	1048.70	1.60	
$[CrNO(CN)_2(py)_2]$	"	"	3.23	943.16	134.00	1077.16	1.62	
$[CrNO(CN)_2(Qu)_2]$	"	"	2.36	925.12	211.00	1136.12	1.66	
$[CrNO(CN)_2(\beta-picoline)_2]$	"	"	2.82	902.40	163.60	1066.00	1.61	
$[CrNO(CN)_2(\gamma-picoline)_2]$	"	"	2.84	908.80	163.60	1072.40	1.62	
$[CrNO(DTC)_2(H_2O)]$	"	"	2.62	1037.52	196.40	1233.92	1.73	
$[CrNO(acac)_2]$	"	"	3.95	1106.00	114.00	1220.00	1.72	
$[CrNO(NCS)_2(dipy)]$	"	"	3.01	1065.54	177.00	1242.54	1.74	
$[CrNO(NCS)_2(dipy)(py)]$	"	"	2.32	1004.56	226.00	1230.56	1.73	
$[CrNO(NCS)_2(o-phen)]$	"	"	2.72	1024.38	200.00	1224.38	1.73	
$[CrNO(NCS)_2(o-phen)(Py)]$	"	"	2.16	987.12	249.00	1236.12	1.74	

than the acetylacetonato derivative. The wide variation
of the nitrogen containing ligands as said earlier suggested
that the polymerisation is not encountered with these lig-
ands as bridging group. It is interesting to note that the
corresponding thiocynato complexes are monomeric (vide
infra) and their magnetic moment values are close to
spin only formula. The infrared spectroscopic results
which will be discussed below, ruled out the possibility
of nitrosyl group interaction or in a bridge position in
these substituted cyano complexes. The alternative possi-
bility of bridging via cyano group is solved using infrared
spectral measurements.

Infrared spectroscopy :-

The infrared spectra of the complexes described
here and of some of the established complexes contain-
ing the $(CrNO)^{2+}$ group are presented in Tables-14,15,16
and 17. A comparison between the starting pentacyanoni-
trosylchromate(I) anion and its derivatives suggested
the appearance of a very strong band in the region
1692-1708 cm^{-1} in these derivatives are coordinated
nitric oxide stretching.[23,117] The shift of ~50 cm^{-1}
for $\nu(NO)$ in these complexes compared to the parent
compound is in agreement for the nonelectrolytic nature
of these complexes where the overall negative charge
on the complex is absent compared to the parent anion.

Table-14.

Important I.R.Spectral bands and their assigments[*]

Compounds	$\nu(NO)$	$\nu(CN)$	$\nu(CrN)$	$\delta(CrNO)$	Reference
$K_3\left[CrNO(CN)_5\right]\cdot H_2O$	1645vs	2137s, 2095sh.	620w	610m	23a
$\left[CrNO(Cl)(diars)_2\right]ClO_4$	1690vs				117
$\left[CrNO(NH_3)_5\right]Cl_2$	1670vs				23a
$\left[CrNO(H_2O)_5\right]Cl_2$	1747vs				23a
$\left[CrNO(MeOH)_5\right]Cl_2$	1719vs				23a
$\left[CrNO(EtOH)_5\right]Cl_2$	1718vs				23a
$\left[Cr(ONO)_2NO(py)_3\right]$	1708vs				23b

[*]Positions (~cm^{-1}) and relative intensities(vs,very strong;m,medium; w,weak; sh,shoulder).

Table-15.

Important I.R.Spectral bands and assignments*

Compound	ϑ(NO)	ν(CN)	Organic ligands	ν(CrN)	δ(CrNO)
[CrNO(CN)₂(o-phen)]	1696vs	2156s, 2125sh	1600s, 1520w, 1500w, 1470m, 1425s, 1370w, 1330w, 1272w, 1225w, 1150w, 1092w, 1060w, 1040w, 1022m, 875m, 850s, 716m, 650m, 608w,	625w	592w
[CrNO(CN)₂(dipy)]	1694vs	2157s, 2133sh.	1594m, 1550w, 1490w, 1482m, 1430m, 1508m, 1228w, 1208w,1175w, 1150w, 1100w, 1075w, 1030w, 1015m, 765s, 715m, 480b.	612w	600w
[CrNO(CN)₂(py)₂]	1700vs	2156s, 2125sh.	1600m, 1530w, 1470w, 1440s, 1375w, 1210m, 1155w, 1076m, 1025w, 1000w, 755m, 695s, 480b.	615w	595w
[CrNO(CN)₂(Qu)₂]	1708vs	2150s, 2125sh.	1600s, 1542m, 1482m, 1445s, 1200m, 1050m, 855m, 770s.	615w	585m

*Positions (/cm⁻¹)and relative intensities (vs,very strong; s,strong; m,medium;w,weak;b,broad; sh, shoulder). Data taken from figures. 3a,3b,4a,4b, 5a and 5b.

$[CrNO(CN)_2 (o-phen)]$
IN KBr PHASE
IN THE RANGE (2500–1300 cm^{-1})

CM^{-1}

FIG. – 3 (q)

ABSORBANCE →

$[CrNO(CN)_2(o-phen)]$

IN KBr PHASE

IN THE RANGE (1200–400 cm^{-1})

FIG. – 3 (b)

ABSORBANCE ⟶

[Cr NO(CN)₂ (di py)]

IN KBr PHASE

IN THE RANGE (2500–1200 cm⁻¹)

CM⁻¹

FIG. – 4 (a)

ABSORBANCE ⟶

$\left[CrNO(CN)_2 (di py) \right]$

IN KBr PHASE

IN THE RANGE $(1300-400 \ cm^{-1})$

CM^{-1}

FIG. - 4 (b)

ABSORBANCE →

$$\left[CrNO(CN)_2 (py)_2 \right]$$

IN KBr PHASE

IN THE RANGE (2500-1200 cm^{-1})

CM^{-1}

FIG. - 5 (a)

ABSORBANCE →

$[CrNO(CN)_2(py)_2]$

IN KBr PHASE

IN THE RANGE $(1300-400 \ cm^{-1})$

FIG. - 5 (b)

CM^{-1}

ABSORBANCE $\longrightarrow$
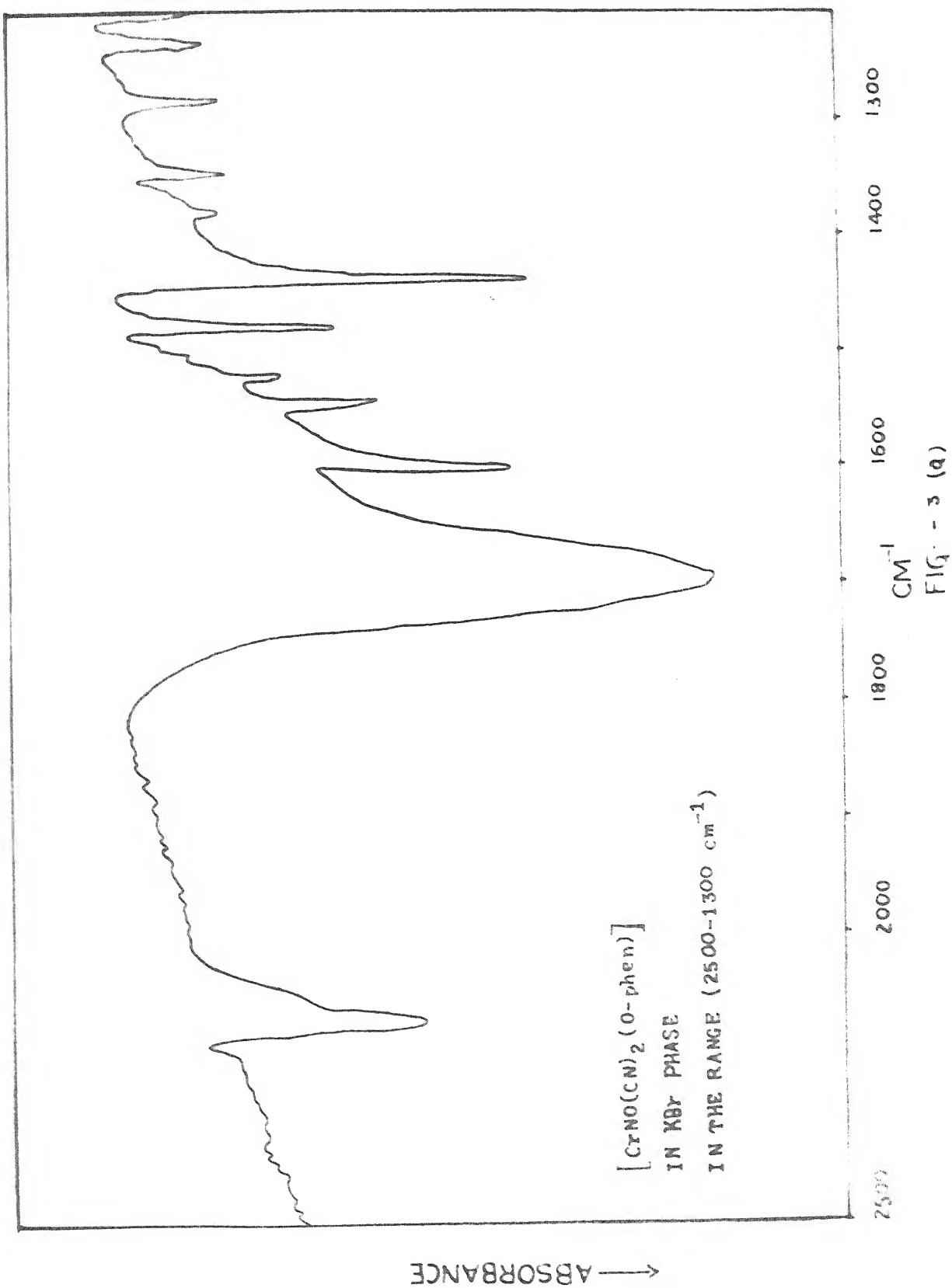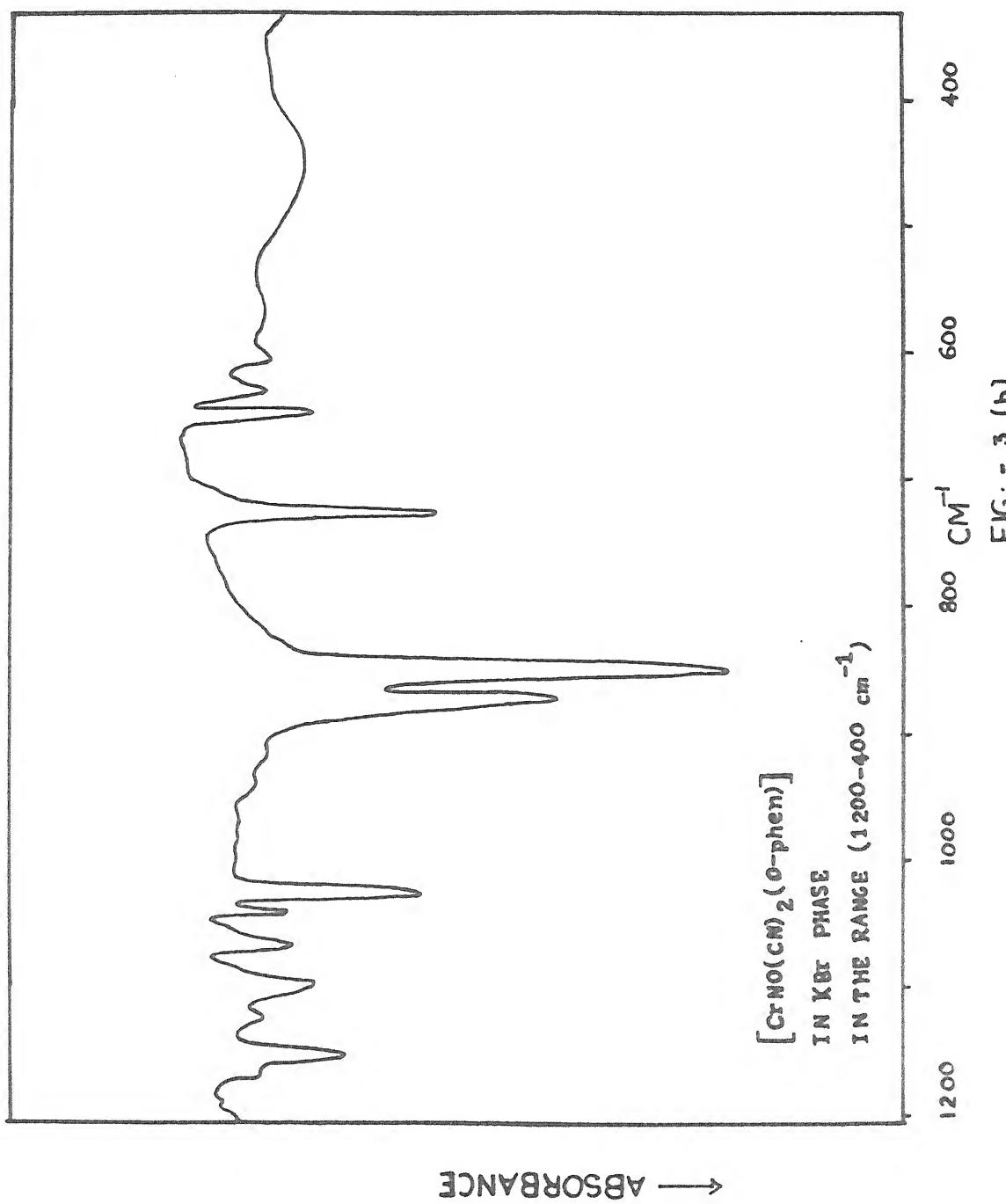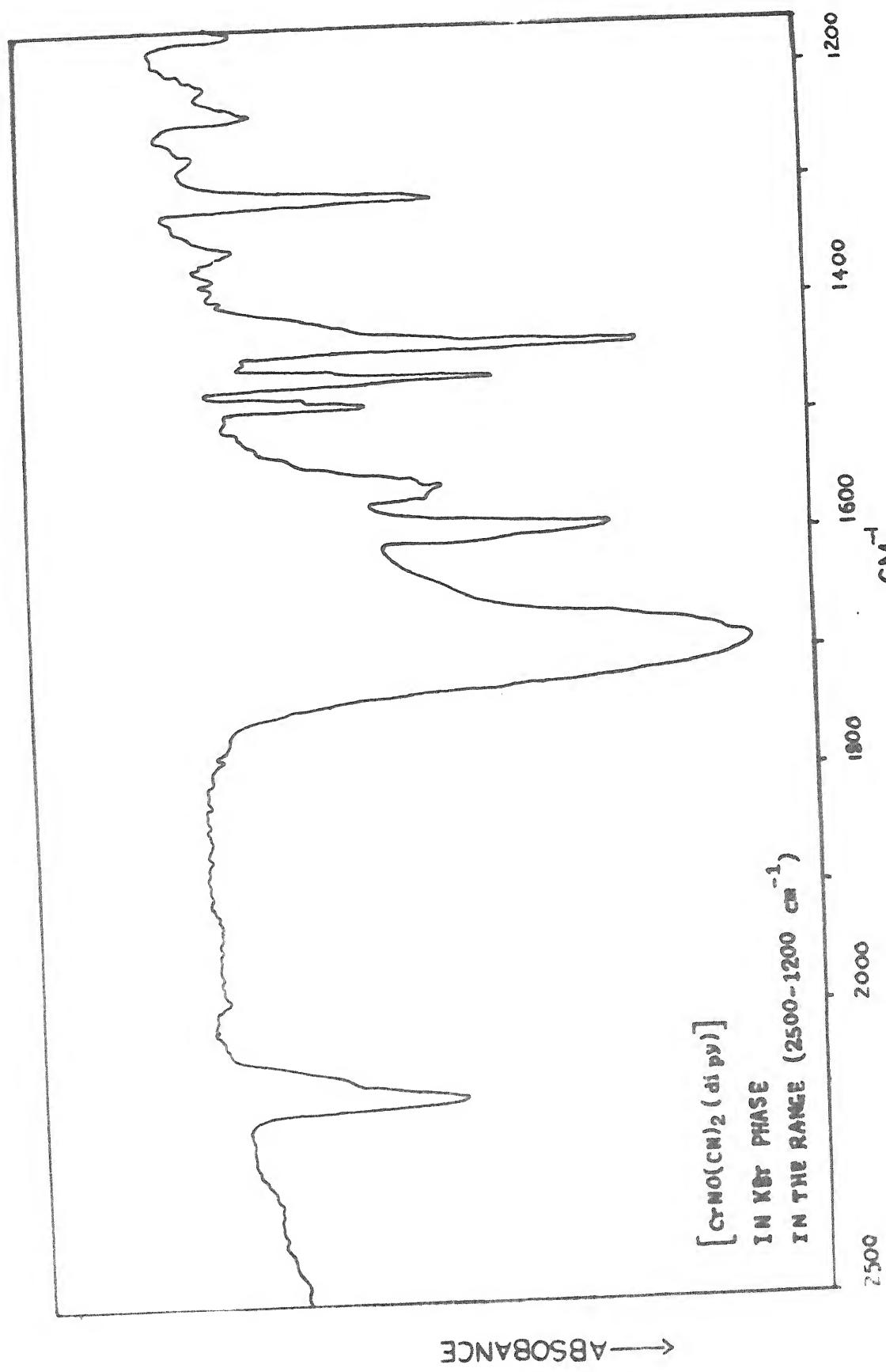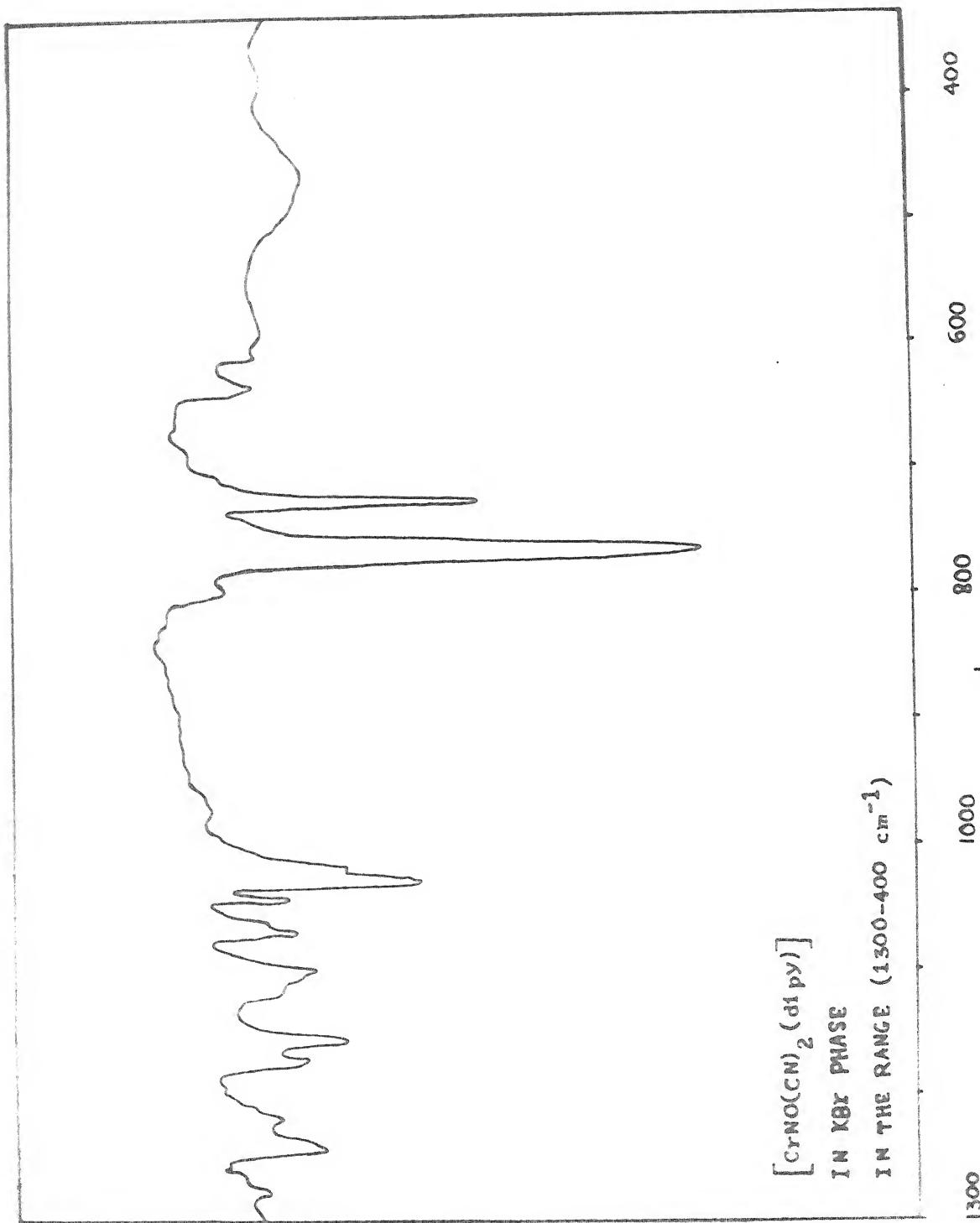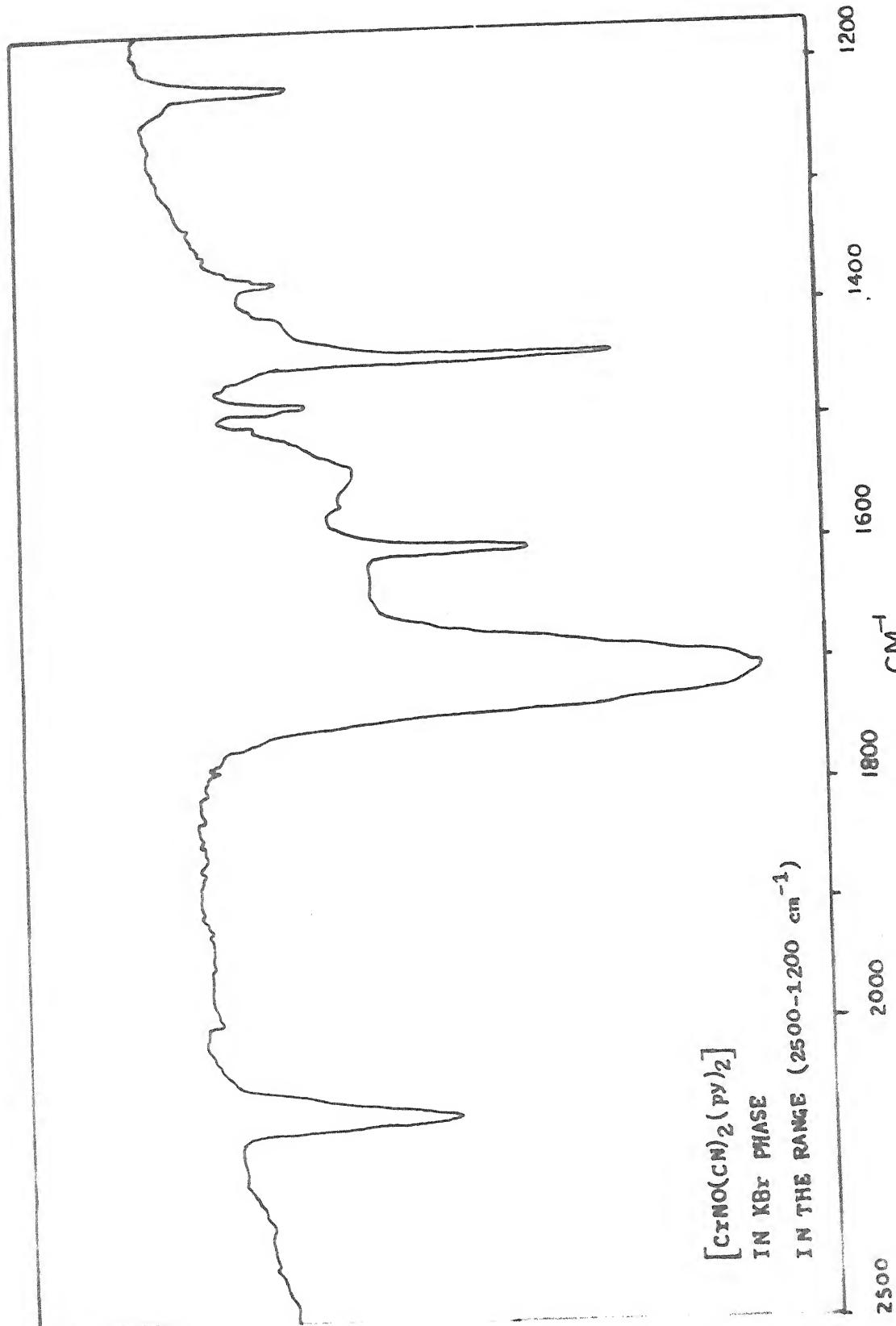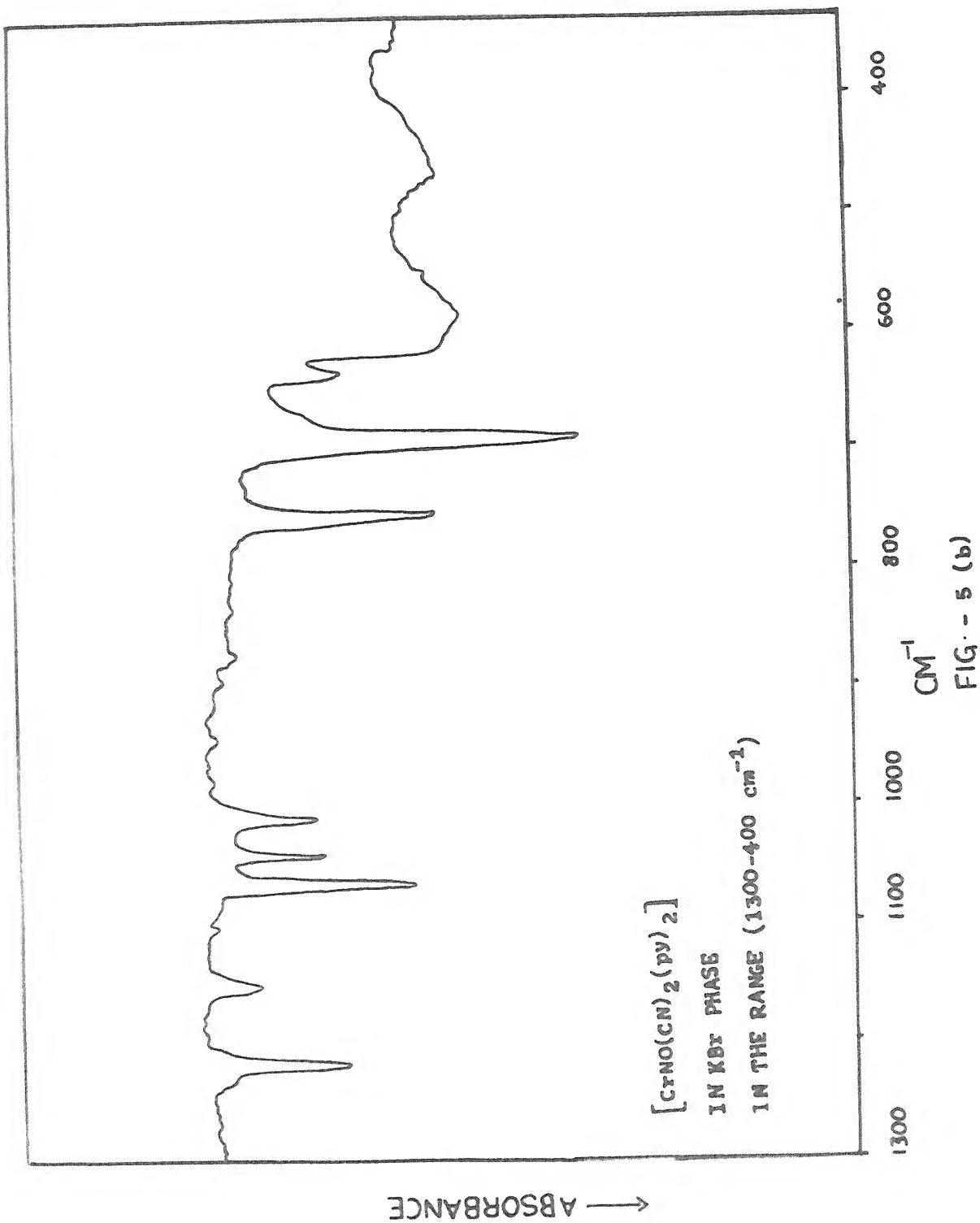
Table-16

Important I.R. Spectral bands and assignments*

Compound	ν(NO)	ν(OH)	δ(H-O-H)	Organic ligands			ν(CrN)	δ(CrNO)
[Cr(NO)(acac)$_2$]	1692vs	-	-	1570w, 1360s, 1000m, 780m, 540w,	1500w, 1250s, 940m, 695m, 415w.	1408w, 1180w, 930m, 676v,	610w	592v
[CrNO(DMC)$_2$(H$_2$O)]	1705vs	3540b, 3480b.	1620sh.	1490m, 1355w, 1205m, 995v, 780w,	1430m, 1300w, 1145m, 910w, 470w.	1375w, 1275m, 1070w, 850w,	620w	575w

*positions (/cm^{-1}) and relative intensities (vs, very strong; s, strong; m, medium; v.weak; b, broad).
Data taken from figures 6a,6b,7a and 7b.

$[CrNO(acac)_2]$
IN KBr PHASE
IN THE RANGE (2000-900 cm^{-1})

FIG. - 6 (a)

ABSORBANCE →

CM^{-1}

2000 1600 1400 1200 900

ABSORBANCE

$\left[CrNO(acac)_2 \right]$

IN KBr PHASE

IN THE RANGE (1000-400 cm^{-1})

1000   800   600   400

CM^{-1}

FIG. - 6 (b)

$[CuEN(H_2O)_2(H_2O)]$

IN KBr PHASE

IN THE RANGE (3600-1600 cm^{-1})

FIG. - 7 (a)

ABSORBANCE →

3500   3000   2500   CM^{-1} 2000   1800   1600
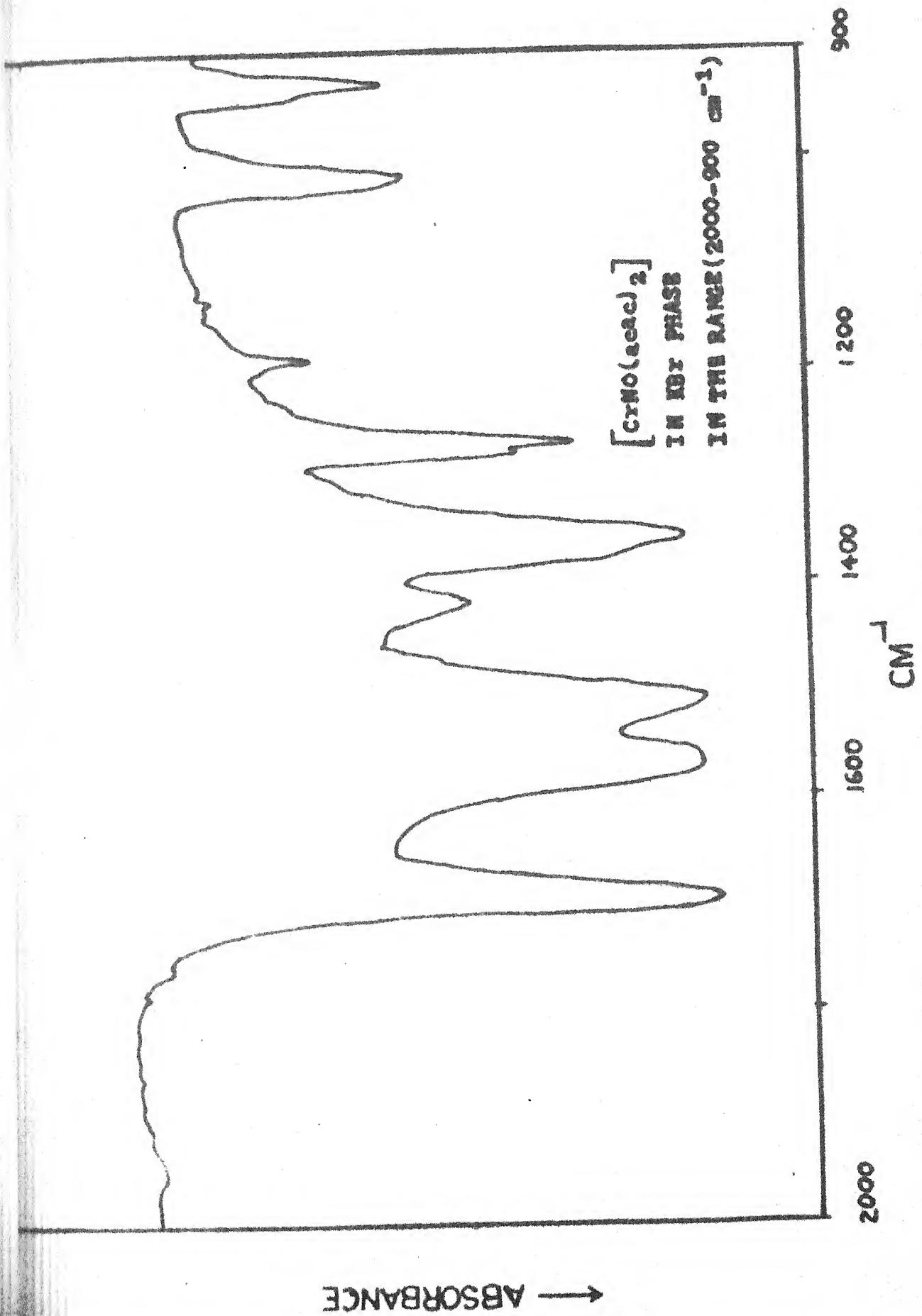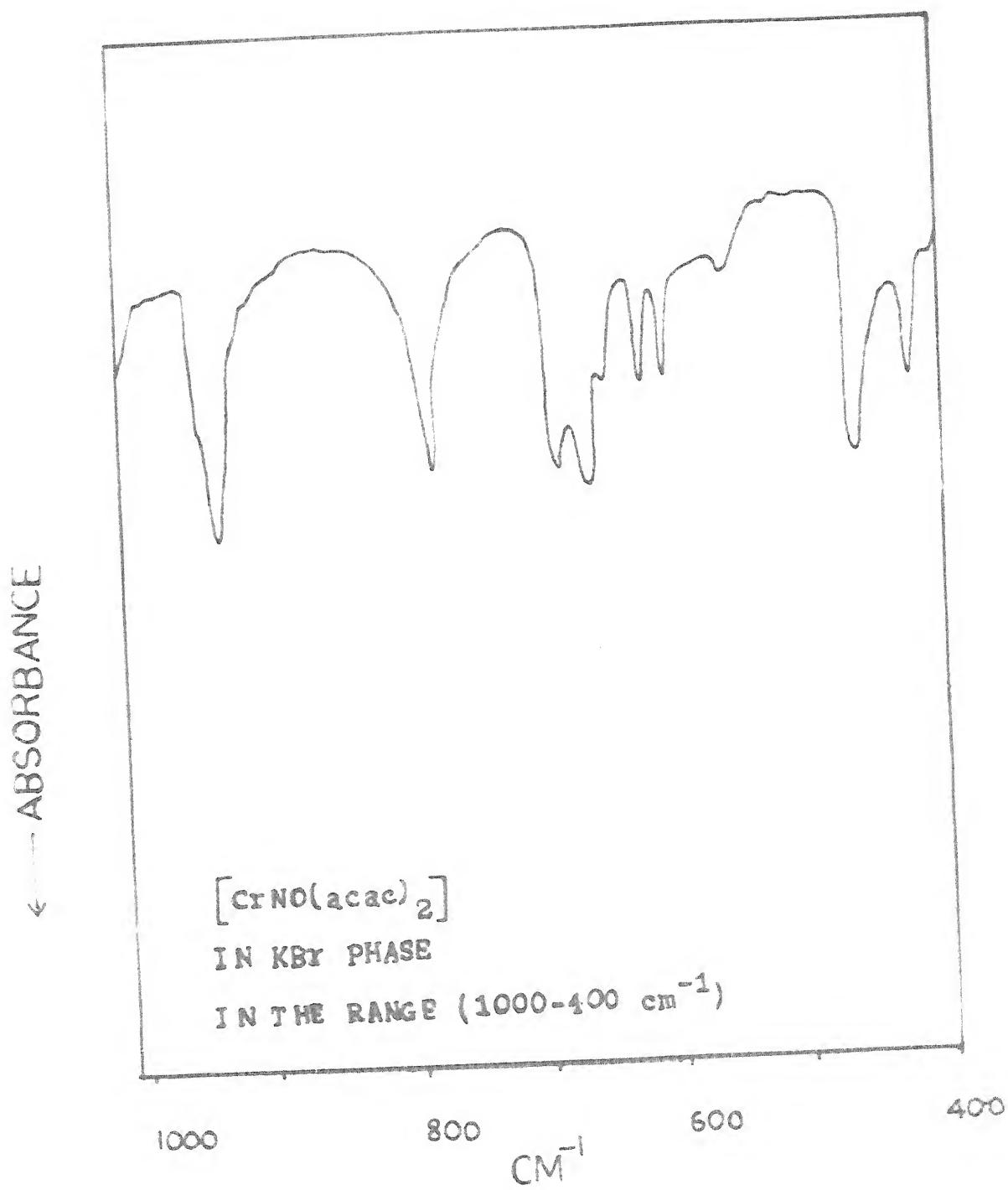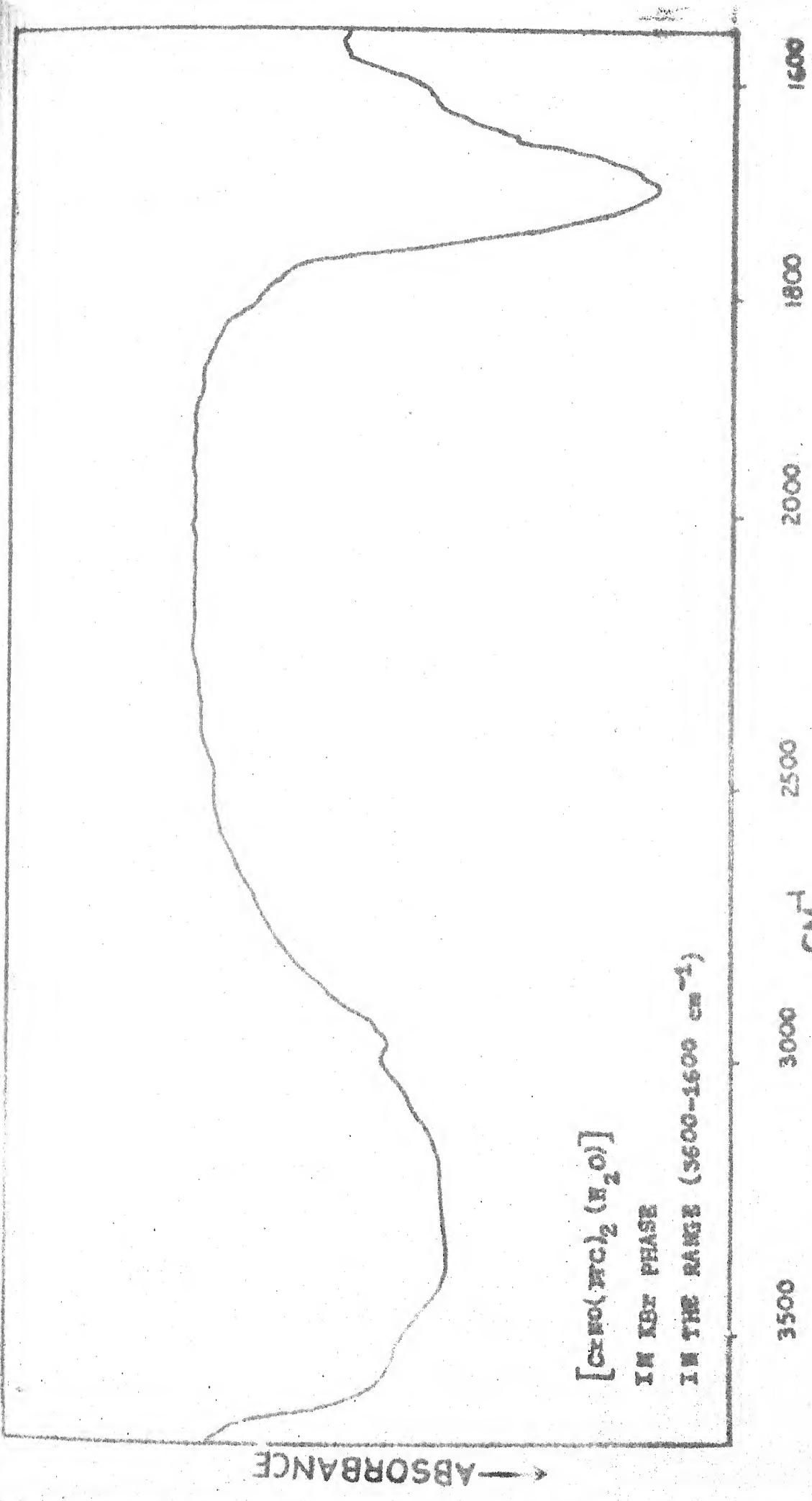
$[CrNO(DTC)_2(H_2O)]$
IN KBr PHASE
IN THE RANGE (1600-400 cm^{-1})
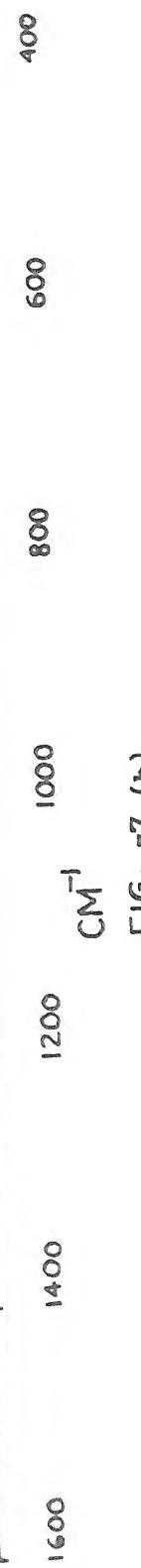
FIG. -7 (b)

Table-12

Important I.R. Spectral bands and assignments*

Compound	ν(NO)	ν(CN)	Organic ligands	ν(CrN)	δ(CrNO)
[CrNO(NCS)₂(o-phen)]	1710s	2070vs	1440w, 1105w, 710m, 1415m, 880w, 685w, 1340w, 845m, 650w. 1220w, 765m, 1145w, 740w,	600w	565w
[CrNO(NCS)₂(o-phen)(py)]	1710s	2080vs	1615w, 1340w, 1145w, 835w, 650m, 1535w, 1315w, 1107w, 770w, 605m, 1515w, 1220w, 1095w, 740w, 460w, 1451w, 1210w, 875w, 725m, 440w, 1425m, 1180w, 845m, 685m,	620m	570w
[CrNO(NCS)₂(dipy)]	1700s	2070vs	1600m, 1372w, 1165w, 1010m, 1576w, 1308m, 1150w, 760s, 1500m, 1295w, 1084w, 715m, 1480m, 1250w, 1070w, 600w, 1440s, 1210w, 1025w,	620w	595w
[CrNO(NCS)₂(dipy)(py)]	1700s	2075vs	1602m, 1310m, 1148w, 800w, 1575w, 1296w, 1088w, 756s, 1495m, 1245w, 1050w, 716w, 1475m, 1215w, 1020w, 600w, 1438w, 1170w, 1014m, 570w.	625w	592w

*Positions (/cm⁻¹) and relative intensities(vs,very strong;s,strong;m,medium; w,weak).

Data taken from figures 8a,8b, 9a, 9b, 10a, 10b, 11a and 11b.

ABSORBANCE →

$[CrNO(NCS)_2(o-phen)]$

IN KBr PHASE

IN THE RANGE ($4000-1600$ cm^{-1})

CM^{-1}

FIG - 8 (a)

$[Cu(ImdazCS)_2(o-phen]$
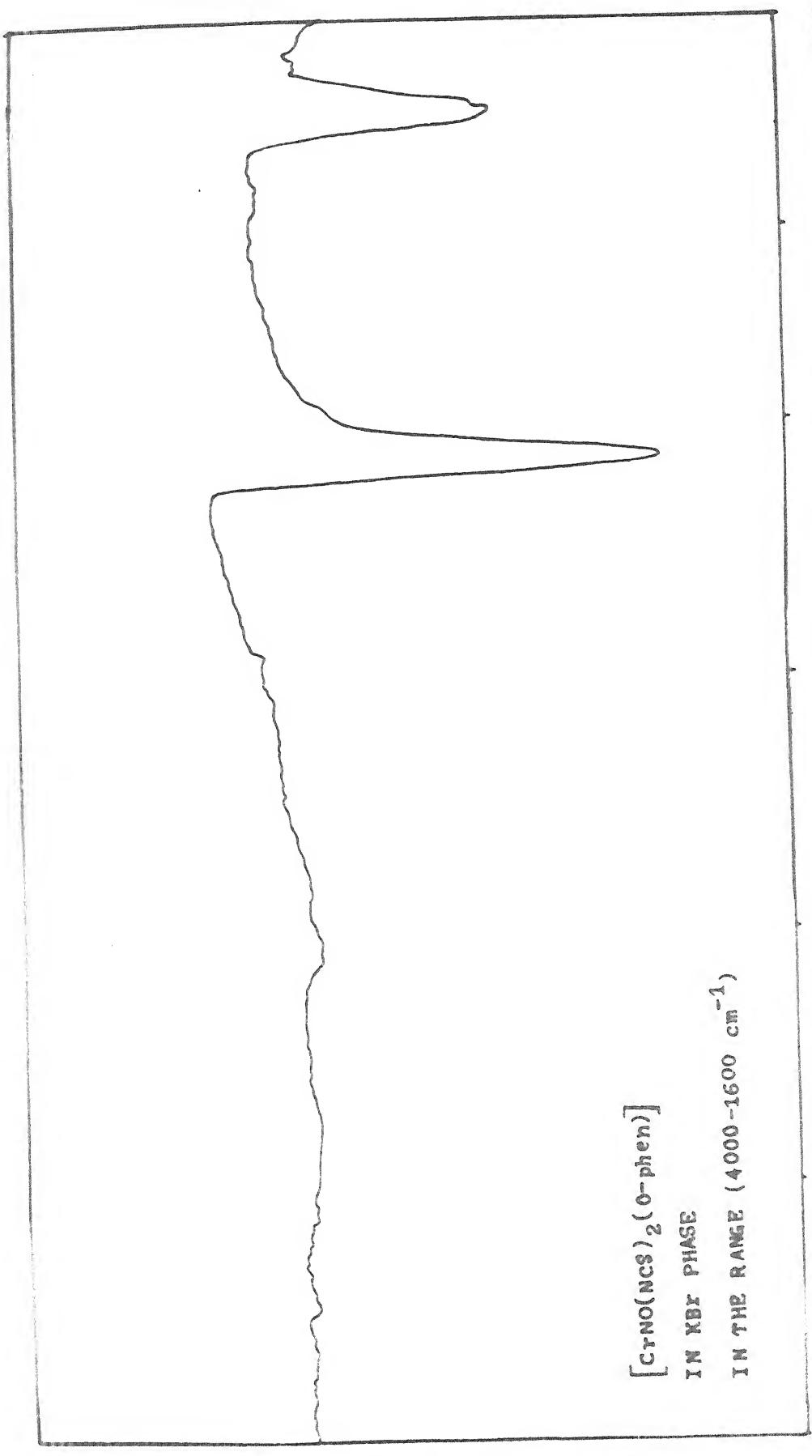
IN KBr PHASE

IN THE RANGE $(1750 \rightarrow 400\ cm^{-1})$

FIG. - 8 (b)

CM^{-1}

ABSORBANCE →

ABSORBANCE →

[Cr HO(NCS)₂(o-phen)(W)]
IN KBr PHASE
IN THE RANGE (3900-1650 cm⁻¹)

CM⁻¹

FIG.- 9 (c)

$$\left[Cr NO (NCS)_2 (O-phen) (py) \right]$$
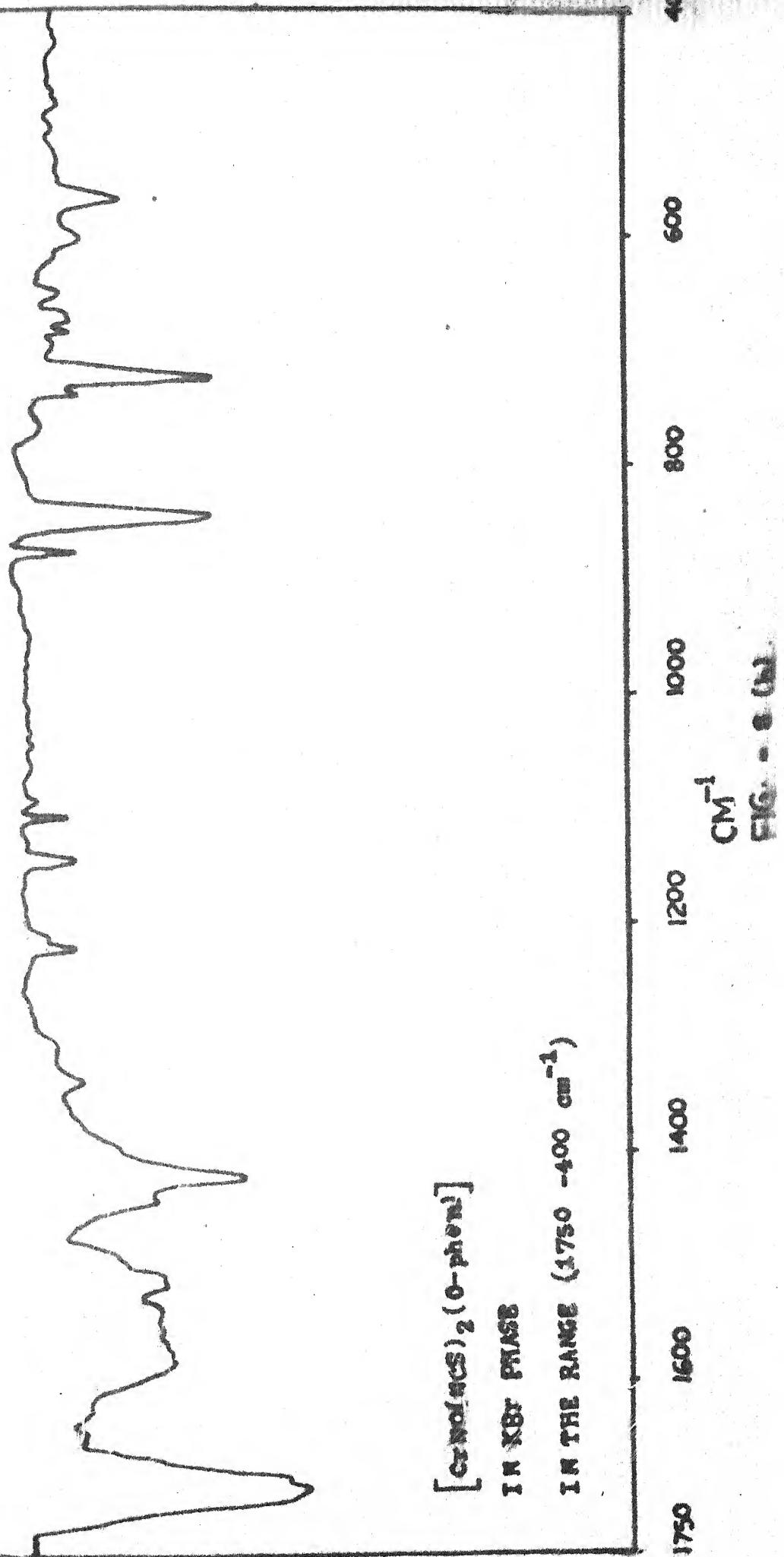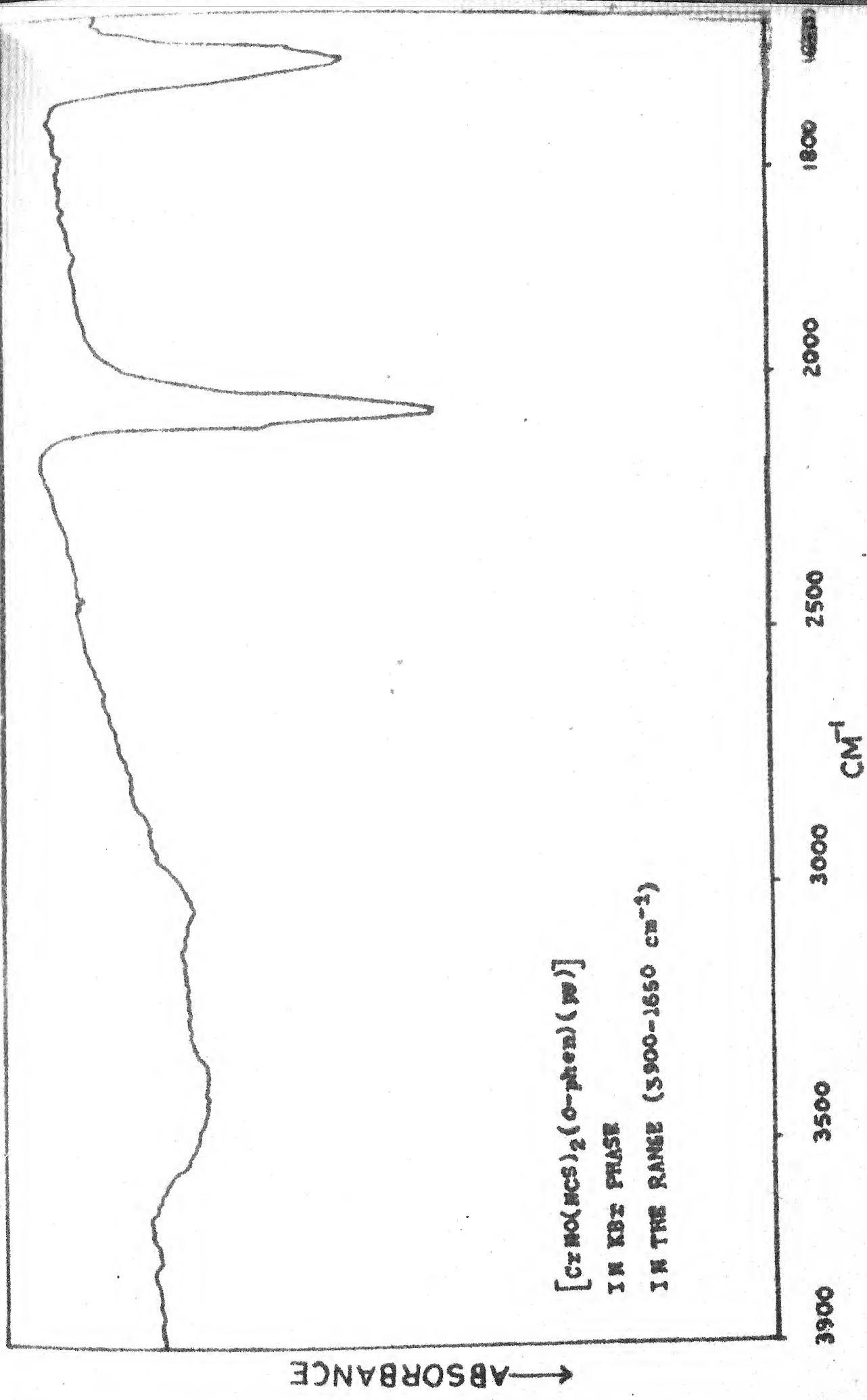
IN KBr PHASE

IN THE RANGE $(1650-400 \text{ cm}^{-1})$
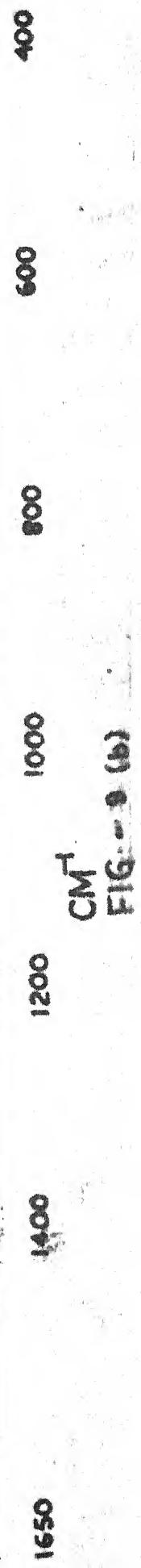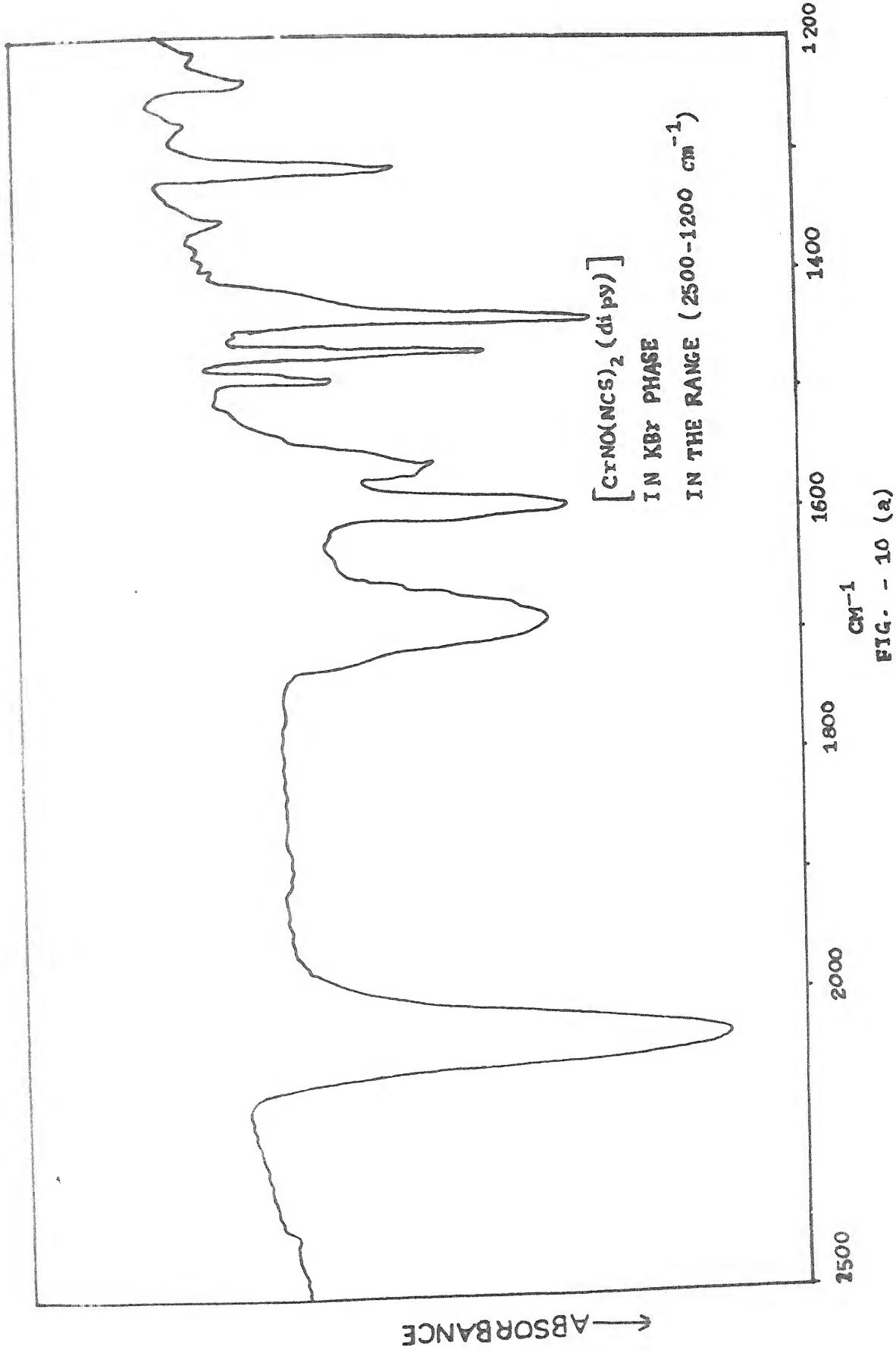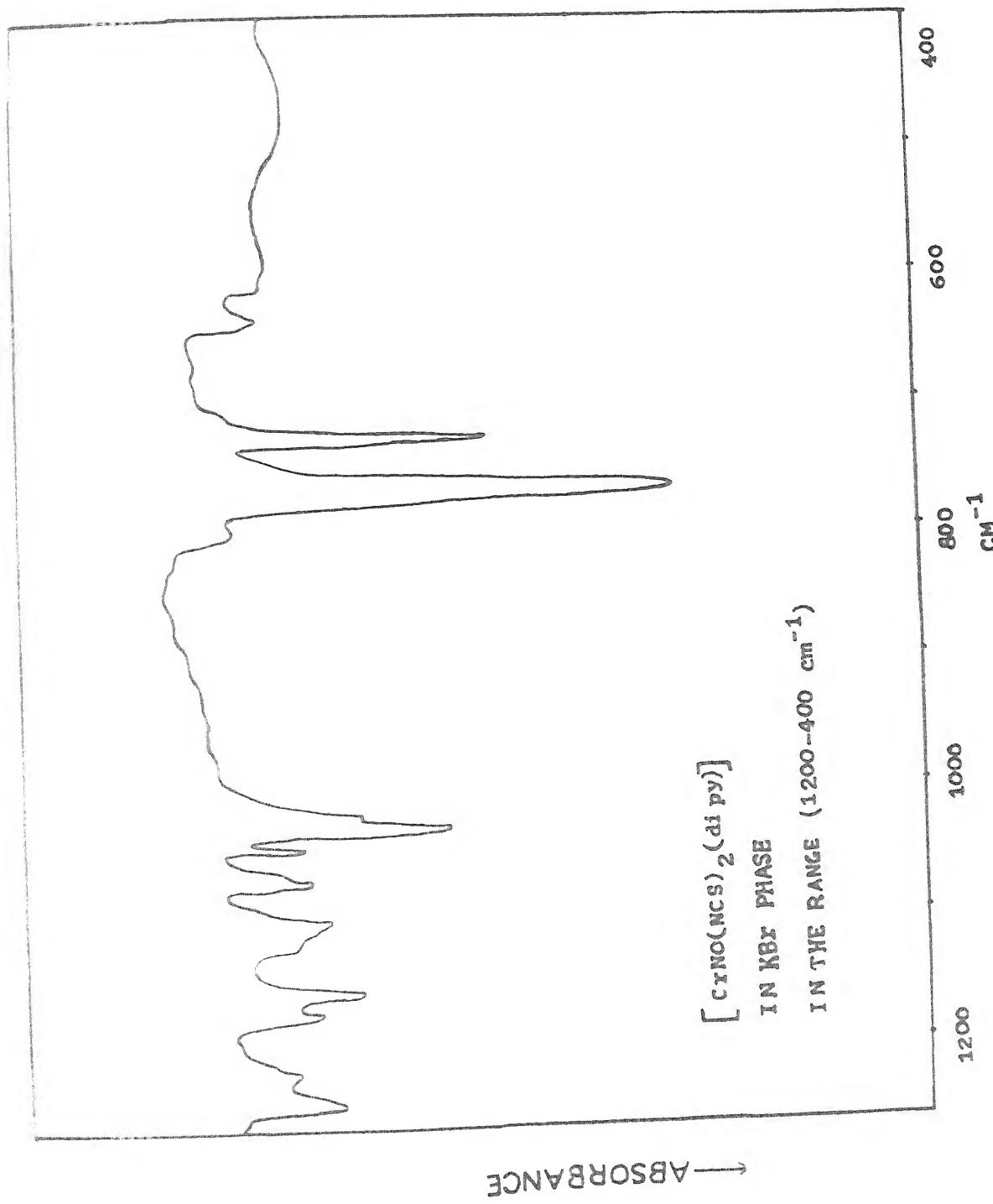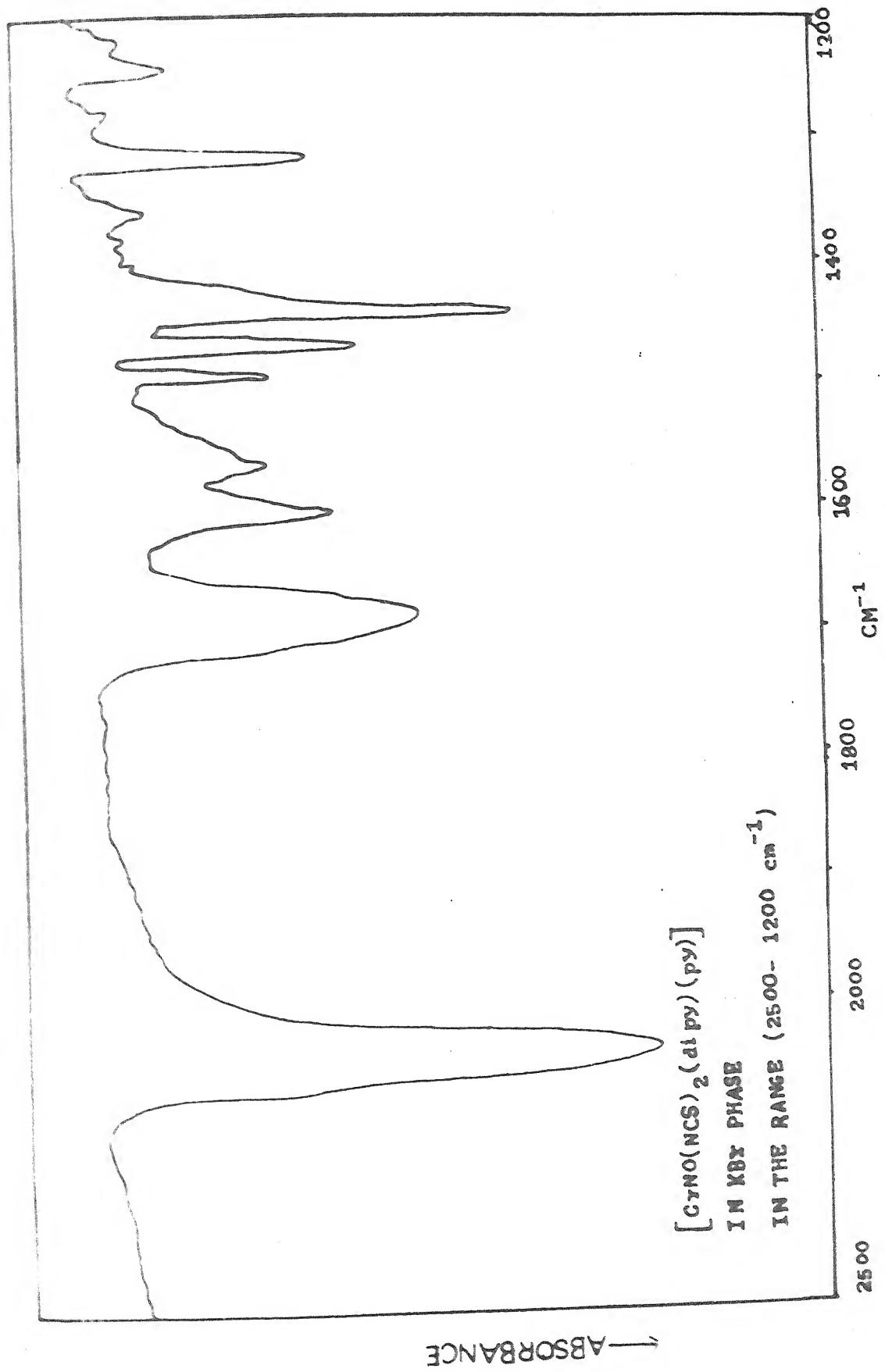
FIG.- 9 (b)

CM^{-1}

ABSORBANCE $\longrightarrow$

$\left[CrNO(NCS)_2 (di\ py) \right]$
IN KBr PHASE
IN THE RANGE $(2500-1200\ cm^{-1})$

CM^{-1}

FIG. - 10 (a)

ABSORBANCE →

ABSORBANCE →

[CrNO(NCS)$_2$(di py)]

IN KBr PHASE

IN THE RANGE (1200—400 cm^{-1})

1200   1000   800   600   400
              CM^{-1}

FIG.- 10 (b)

$[C_7NO(NCS)_2(dipy)(py)]$

IN KBr PHASE

IN THE RANGE (2500- 1200 cm^{-1})

FIG. - 11 (a)

CM^{-1}

←ABSORBANCE→

$[CoHo(NCS)_2 (\alpha 1 py)(py)]$

IN KBr PHASE

IN THE RANGE (1300- 400 cm^{-1})

FIG.- 11 (b)
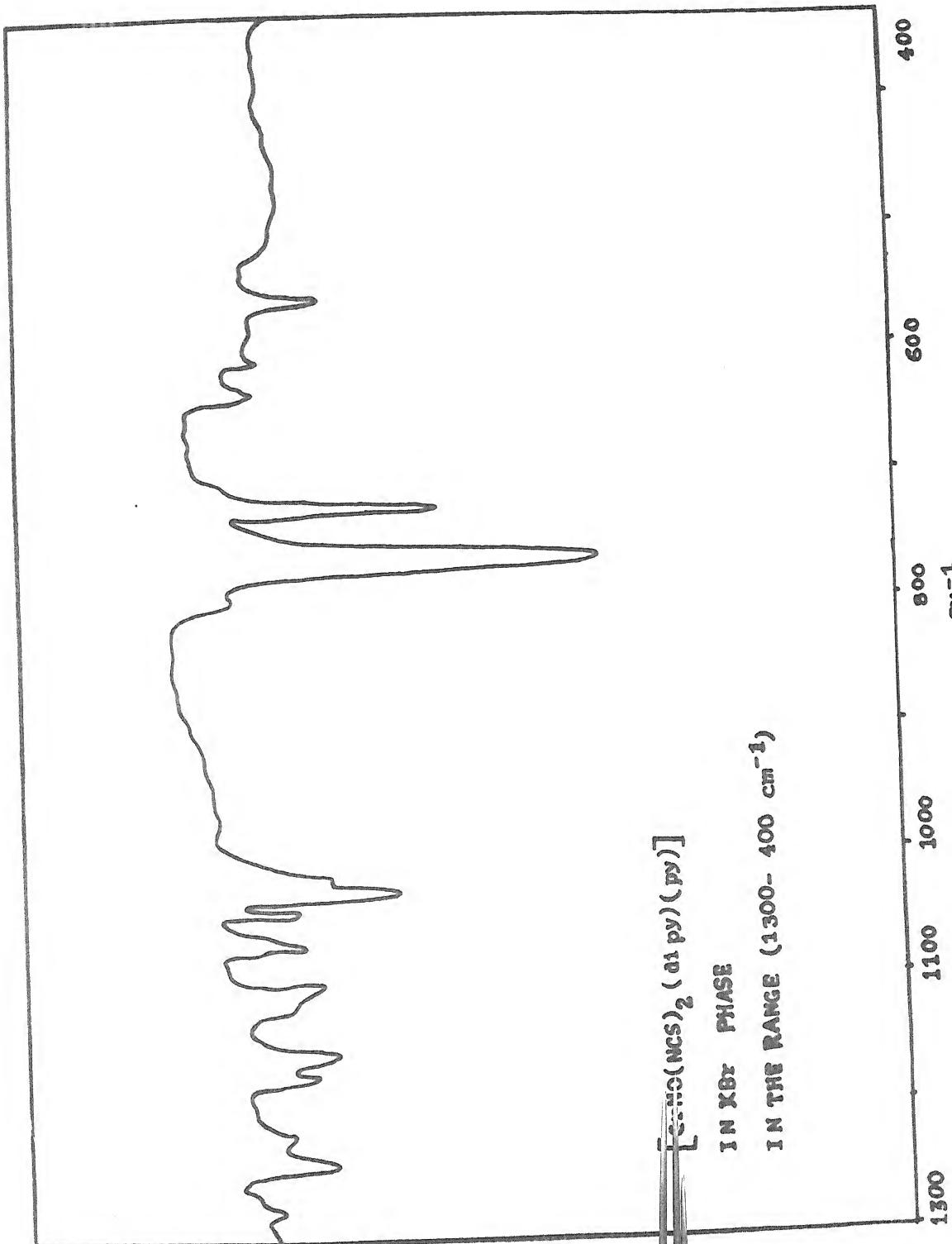
A further possibility of this shift may be due to (a) change in coordination number (b) the change in the nature of co-ligand in respect to π-bonding capacity. In the series of heterocyclic aromatic amines and imino derivatives some trend is observed. In the dipyridyl and o-phenanthroline the ν(NO) remain almost identical which is slightly lower in frequency to that for the complexed pyridine or quinoline. This suggests that in the chelated derivatives metal-nitrogen bond becomes stronger compare to non-chelated derivatives. Though dipyridyl and o-phenanthroline are generally shown to be better π-bonding ligand compare to pyridine or quinoline the trend we follow here is abit different. The N-L stretching for the acetylacetonato complex appears almost identical to that in dipyridyl and o-phenanthroline complexes. This suggests that the N-L stretching remains unaffected with the change of donor atoms of the ligand used. This is in accordance with the proposition made by Enemark and Feltham.[51] The electronic effect of the metal ion and the coordinated NO group should not be treated as separable entity rather the (CrNO) group can be treated as "inorganic functional group".[51] However the position of appearance of ν(NO) in these complexes can be treated in the light of the parent complex as the terminal bonded

containing the linear Cr-NO group, thus ruled out the
possibility of nitrosyl group to act as bridging
group. Hence the polymeric nature of the cyano subs-
tituted complexes as supported by their generalinsolubility
in different common solvents, their resistivity in alky-
ltion reaction (vide experimental section) and their un-
usual low magnetic moment values along with broadening
in e.s.r. spectra (vide infra) can be accounted for by
presuming a cyano bridged structure as shown in fig.2a,
2b, 2c and 2d. Solid state spectra of all these deriva-
tives show two cyanide stretchings appearing in identical
positions that is at 2150-2157 and at 2125-2133 cm^{-1}.
The lower band appears as shoulder in all the cases. In
bridged cyano complexes, the bridging is encountered
only in the form of $N-C \equiv N-M'$, which results $\nu(CN)$
to shift to a higher frequency[42]. We assign the $\nu(CN)$
at 2150-2157 cm^{-1} for the bridging cyano groups and the
rest one for each complex for the terminal cyano groups
(fig.2). However four possibilities exist for the
bridge structure (fig. 2a,2b, 2c and 2d). Fig.2a and
2b represent a dimeric structure satisfying a hexacoo-
rdination of the central metal using cyano bridged stru-
cture. Fig.2c and 2d represent a tetrametic structure
leading to hexacoordinated structure of the central
metal with cyanide bridge. The dimeric structure is
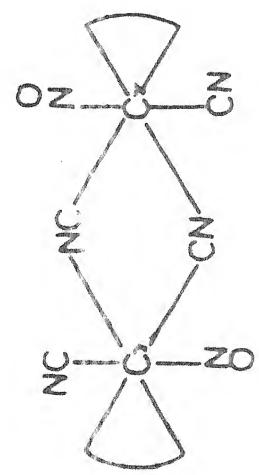
FIG·2(a)

FIG·2(b)

= dipy, o-phen, 2py, 2qu, 2pic
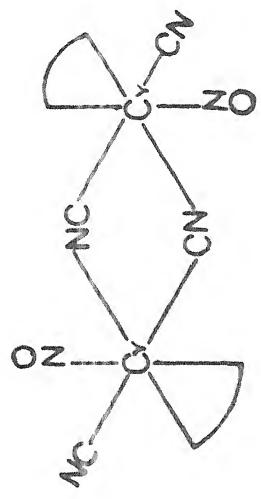
FIG·2(c)
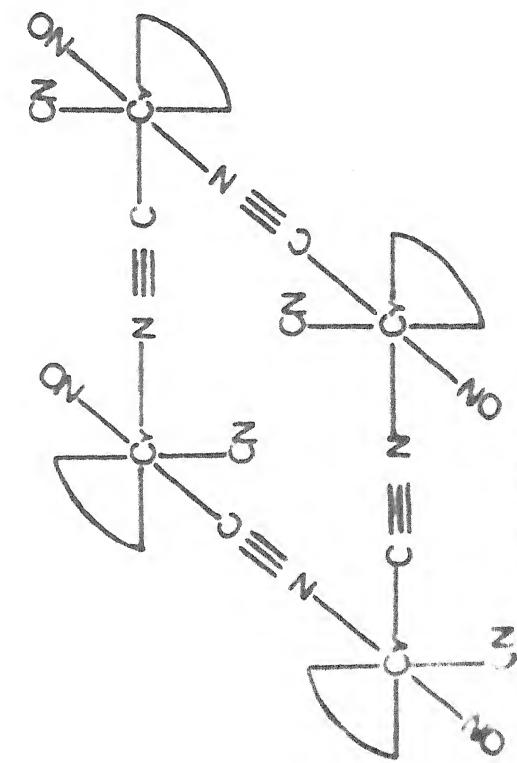
FIG·2(d)
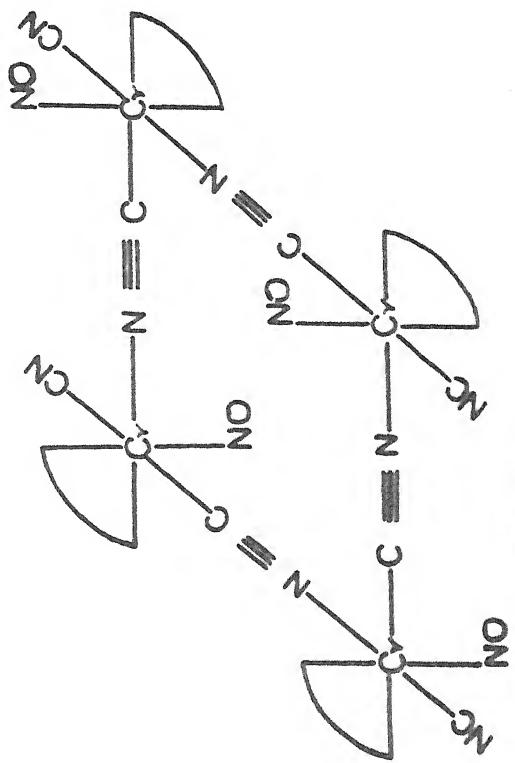
unfavourable in the sense that here a linear arrangement of the cyano bridge moiety is not possible. The other reported cyano bridge complexes contain only the linear attachemtn $M-C\equiv N-M'$ [42]. Recently Bustin [118] through electrochemical studies on the reaction of $[Cr(CN)(H_2O)_4NO]^+$ with Ag^+ and Hg^{2+} ions proposed that the bridge structure like $Cr-N-C-M$ $(M/=Ag^+, Hg^{2+})$ is formed. The CN bridged linkage isomer like $Cr-C-N-M$ $(M=Hg^{2+})$ has also been characterised. Thus in accordance with the linear cyano bridge structure, the tetrameric structures (fig.2c and 2d) are favourable. It has been shown by Raynor and coworkers [115] that in acid hydrolysis of pentacyanonitrosyl-chromate(I) anion, the first aquation takes place to the cyanide group in axial position that is trans to the nitrosyl group. Taking into account of this trans dire-cting effect of the nitrosyl in the tetrameric structures, the structure, 2d is untenable. Hence all these evidences are in conformity with the structure, 2c.

In aquo bis (diethyldithiocarbamato)nitrosyl(I) chromium(I), a slightly higher $\nu(NO)$ compare to that of bis(acetylacetonato)nitrosylchromium(I)(Table-16) is in conformity to the e.s.r. result (vide infra). It is known that lower coordination number, higher the observed frequencies and the reverse trend observed as described in the preceeding lines further support that

dithiocarbamate is a better complexing ligand than the acetylacetonate.

In the thiocyanato substituted complexes the infrared spectral bands and their tentative assignments are presented in Table-17. The thiocyanate group may coordinate to the metal through either the nitrogen or the sulphur atom or both. Chromium being in the first transitional series, has been placed as class A metal[119]. On coordination the $\nu(CN)$ frequency of NCS^- is lowered in N-bonded complexes than in the S-bonded complexes[120]. A comparison of the observed cyanide stretching with those of the known thiocyanato complexes[42] suggest N-bonded thiocyanate group in these complexes. The use of $\nu(CS)$ to say more about the nature of coordination could not be possible here because of the presence of several other bands originated from the organic ligands in this region. However, the greater complexity in the e.s.r. spectra of these complexes (vide infra) suggests the coordination through nitrogen.

A comparison with the corresponding substituted cyano complexes, for example, $[CrNO(CN)_2(o\text{-phen})]$ with $[CrNO(NCS)_2(o\text{-phen})]$ is highly interesting. The former is proposed to be polymeric in nature whereas the latter is a monomer. This difference may be attributed due to the lack of chromium to coordinate through

sulphur of the thiocyanato group. This is expected
regarding the classification of chromium as a class
A[119] metal.

$\nu(CrNO)$ and $\delta(Cr-N-O)$ vibration :-

As discussed in the introduction (vide supra),
the complete assignment of these vibrations require
isotope substitution data supplemented by Raman Spectra.
For nitrosyl complexes the complete agreement of the
vibrational spectra through analyses has been achieved
only with $\{RuNO\}^6$ complexes [121-127]. The controversy on
the assignment of these vibrations have been settled,
the $\nu(RuNO)$ be assigned to a band around 600 cm^{-1} and
$\delta(Ru-N-O)$ has been assigned at some what lower frequency,
though sub-reversal of the assignments are reported[123].

Among the complexes described here the
bis(acetylacetonato)nitrosylchromium(I) shows somewhat
clear spectrum (fig.14). In the range 700-385 cm^{-1} a
few sharp bands are observed in acetylacetonato complex
which are consisted mainly in three band envelopes.
The first envelope contains sharp bands at 675,654,
640 cm^{-1}, the second at 610 and 592 cm^{-1} and the
third one at 454 and 412 cm^{-1} respectively. The nature
of the first and third envelopes are identical to that
observed by Mikami and coworkers[128] for several square
planar acetylacetonato complexes of bivalent metals.

The bands in second envelope then should be due to Cr-N streaching and Cr-N-O bending vibrations respectively as reported by Miki[40]. For complexes containing nitrogen donors and dithiocarbamato complex, the appearance of bands at similar wave numbers could not be assigned with certainty as these aromatic bases and dithiocarbamate have their vibrations which appear at similar wave numbers, thus complicating these assignments. However, tentative assignments can be made for bands appeared in the range 585-596 cm^{-1} and 624-612 cm^{-1} for Cr-N-O bending and Cr-N stretching vibrations for these complexes.

Organic ligands vibrations :-

That the organic molecules in the complexes are coordinated to chromium is indicated by shifts in the ligand bands in the spectra of the complexes from their positions in the spectra of the free ligands. Similar shifts on complexation have been characterised in several metal complexes using these ligands.[42,129,130]

Electron spin resonance Spectra :-

The e.s.r. data of the synthesised complexes are presented in Table-19. The reported values for the earlier known complexes are also set out in Table-18. The monomeric bis(acetylacetonato)nitrosylchromium(I) shows some interesting features. Its spectra as powdered sample and diluted in KBr (fig.12a) show a tetragonal distortion

Table-18

Electron spin resonance parameters for known $(CrNO)^{2+}$ complexes.

Complex	g(av)	A(n),G	Reference
Trans- $[CrNO(Cl)(diars)_2]ClO_4$	2.00	5	131
$[CrNO(CN)_5]^{-3}$	1.99	5.3	132
$[CrNO(NH_3)_5]^{2+}$	1.98	6.98	133
$[CrNO(H_2O)_5]^{2+}$	1.97	6.4	133
$[CrNO(CNS)_5]^{3-}$	1.970	-	26

Table-19.

Electron spin resonance parameters for $(CrNO)^{2+}$

complexes

Complex	g(av)	A(n),G
$[CrNO(CN)_2 (o-phen)]$ undiluted in powder form	1.980	
$[CrNO(acac)_2]$ in ethanol	1.987	5.6
$[CrNO(acac)_2]$ in ethanol with pyridine	1.990	
$[CrNO(acac)_2]$ diluted with KBr	1.970 $g\perp = 1.990$ $g_\parallel = 1.951$	
$[CrNO(acac)_2]$ undiluted in powder form	1.980	
$[CrNO(DTC)_2(H_2O)]$ undiluted in powder form	1.990	
$[CrNO(NCS)_2 (o-phen)]$ undiluted in powder form	1.970	
$[CrNO(NCS)_2 (o-phen)(py)]$ undiluted in powder form	1.978	

ESR SPECTRUM OF $[(CrNO(acac)_2]$

SOLID LINE - DILUTED WITH -- KBr

BROKEN LINE- POWDERED PURE SAMPLE

1cm = 15G

3570G

DPPH
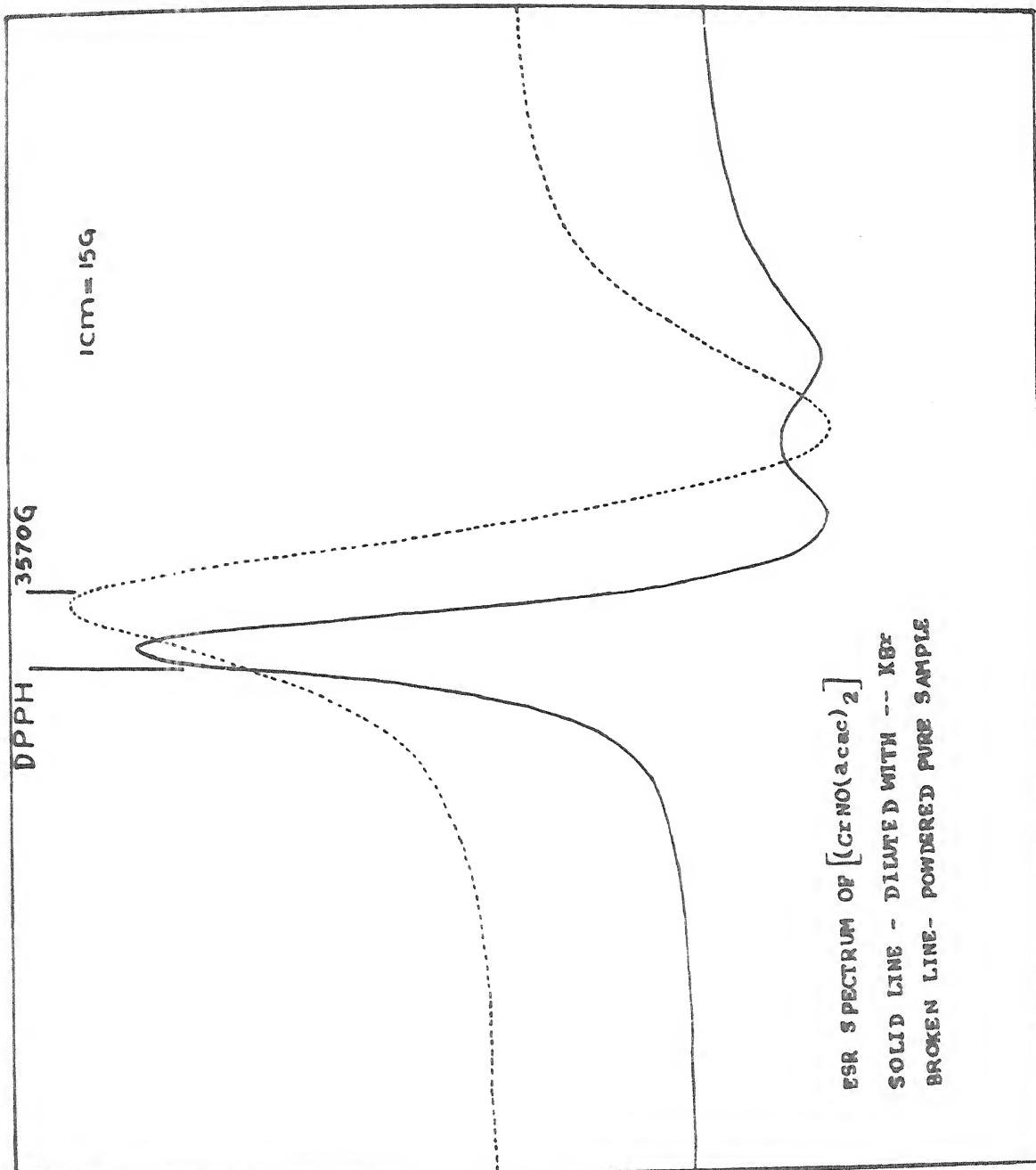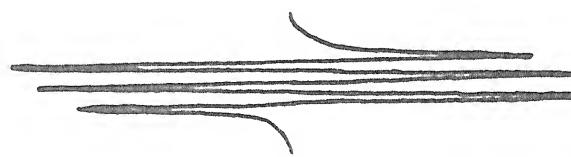
FIG. - 12 (a)

1 cm = 15 G

ESR SPECTRUM OF $[Cr NO(ac ac)_2]$ IN METHANOL

FIG. - 12 (b)

1 cm = 15 G
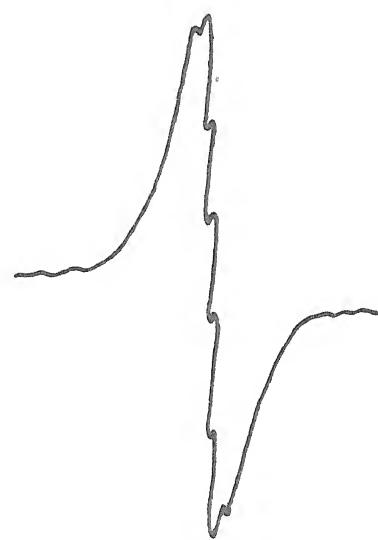
ESR SPECTRUM OF $[CrNO(acac)_2]$
IN PYRIDINE- METHANOL

FIG .- 12 (c)

1 cm = 15 G

ESR SPECTRUM OF $[CrNO(NCS)_2 (o-phen)]$
IN ETHANOL

FIG. - 13

ICM = 15G

3570

ESR SPECTRUM OF
[C, NO(DTC)$_2$(H$_2$O)]
UNDILUTED IN POWDER
FORM

FIG·14

ESR SPECTRA OF
(—) $[C_2 NO(CN)_2 (o\text{-}phen)]$ &
(⋯) $[C_v NO(NCS)_2(o\text{-}phen)]$
UNDILUTED IN POWDER
FORM

$1CM = 15G$

3570

FIG-15(a)

ESR SPECTRUM of

1cm = 15G

3570

ESR SPECTRUM OF
[Cr NO(NCS)$_2$ (o phen)(py)]
UNDILUTED IN POWDER
FORM

1cm = 15G

3570
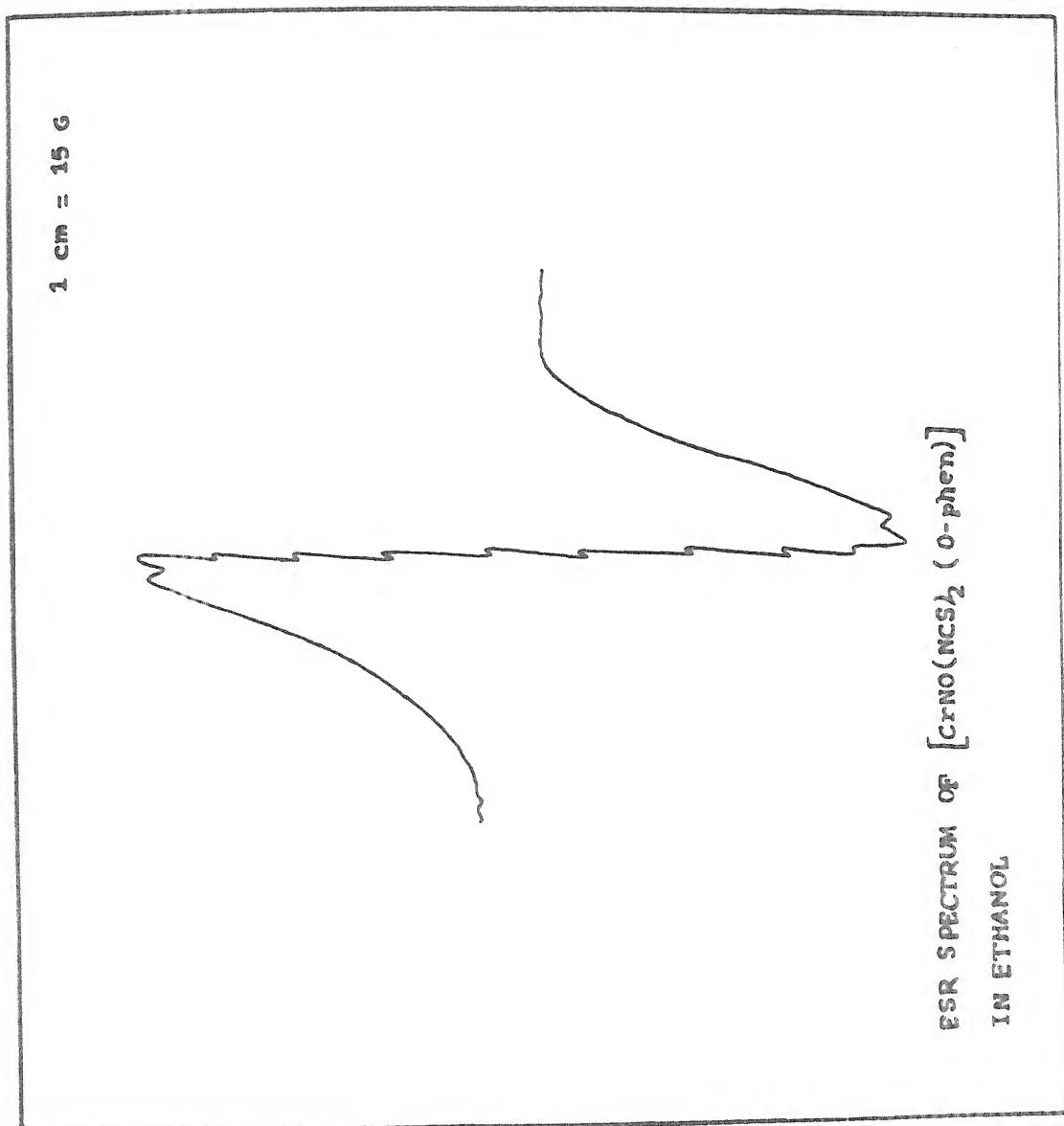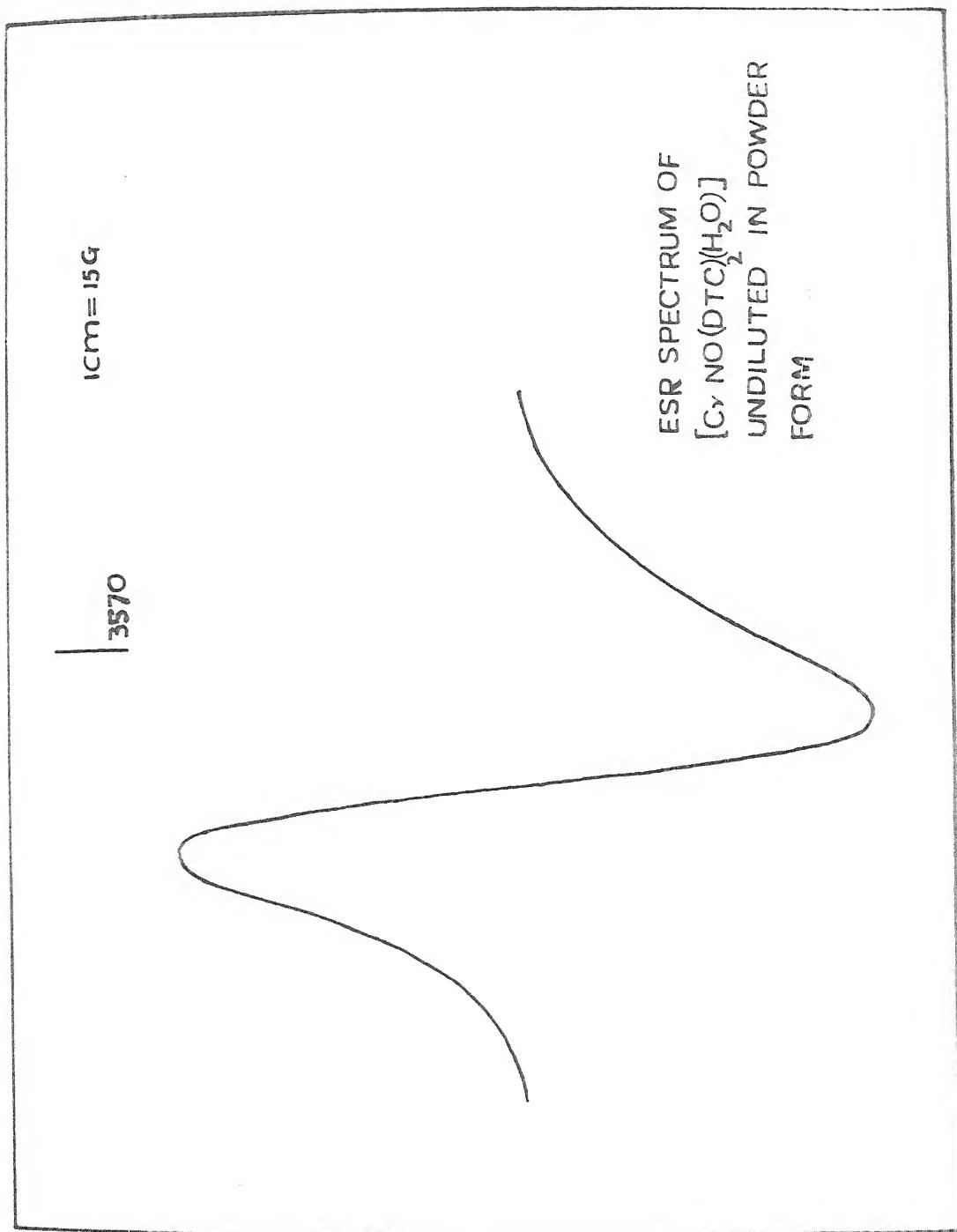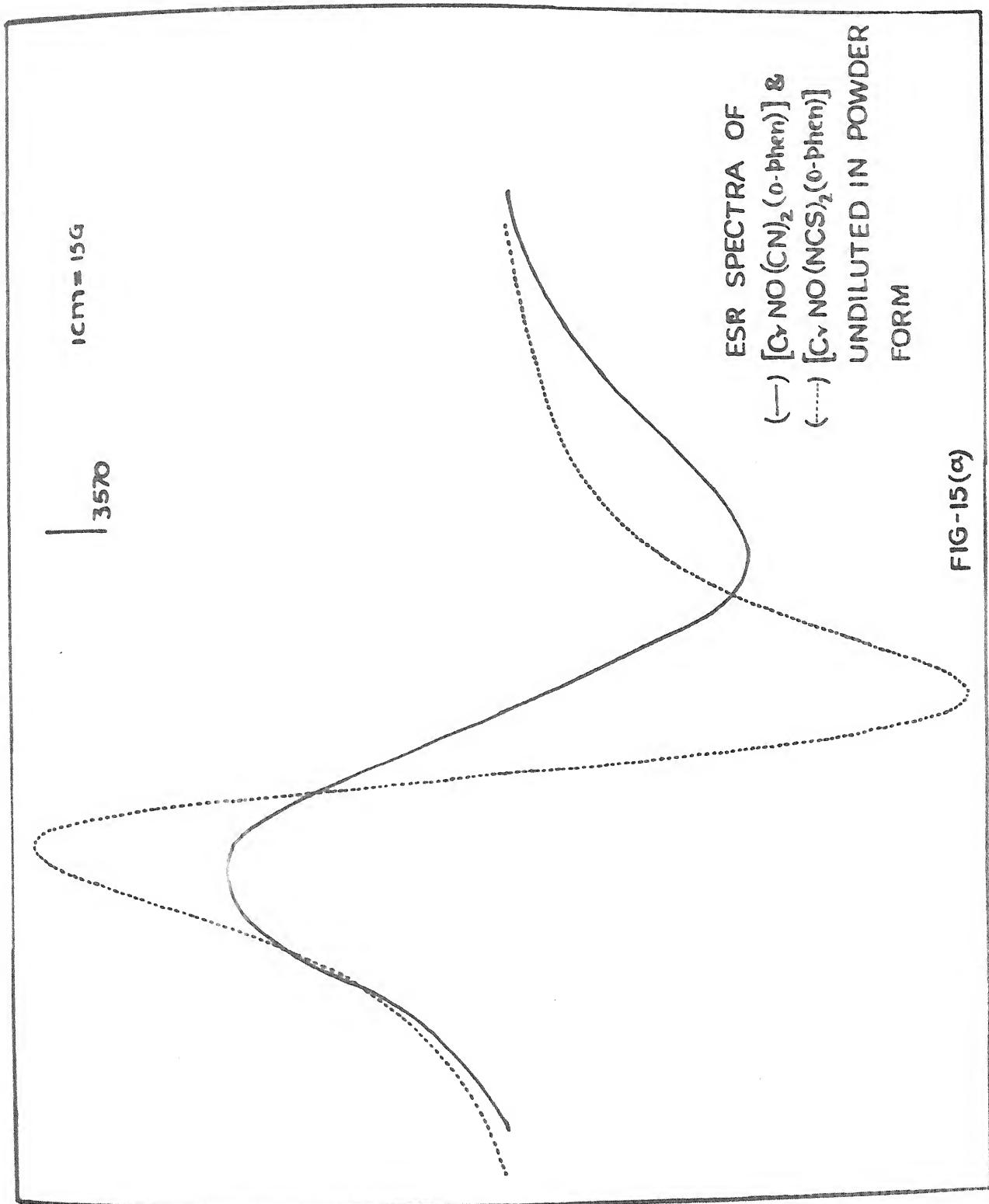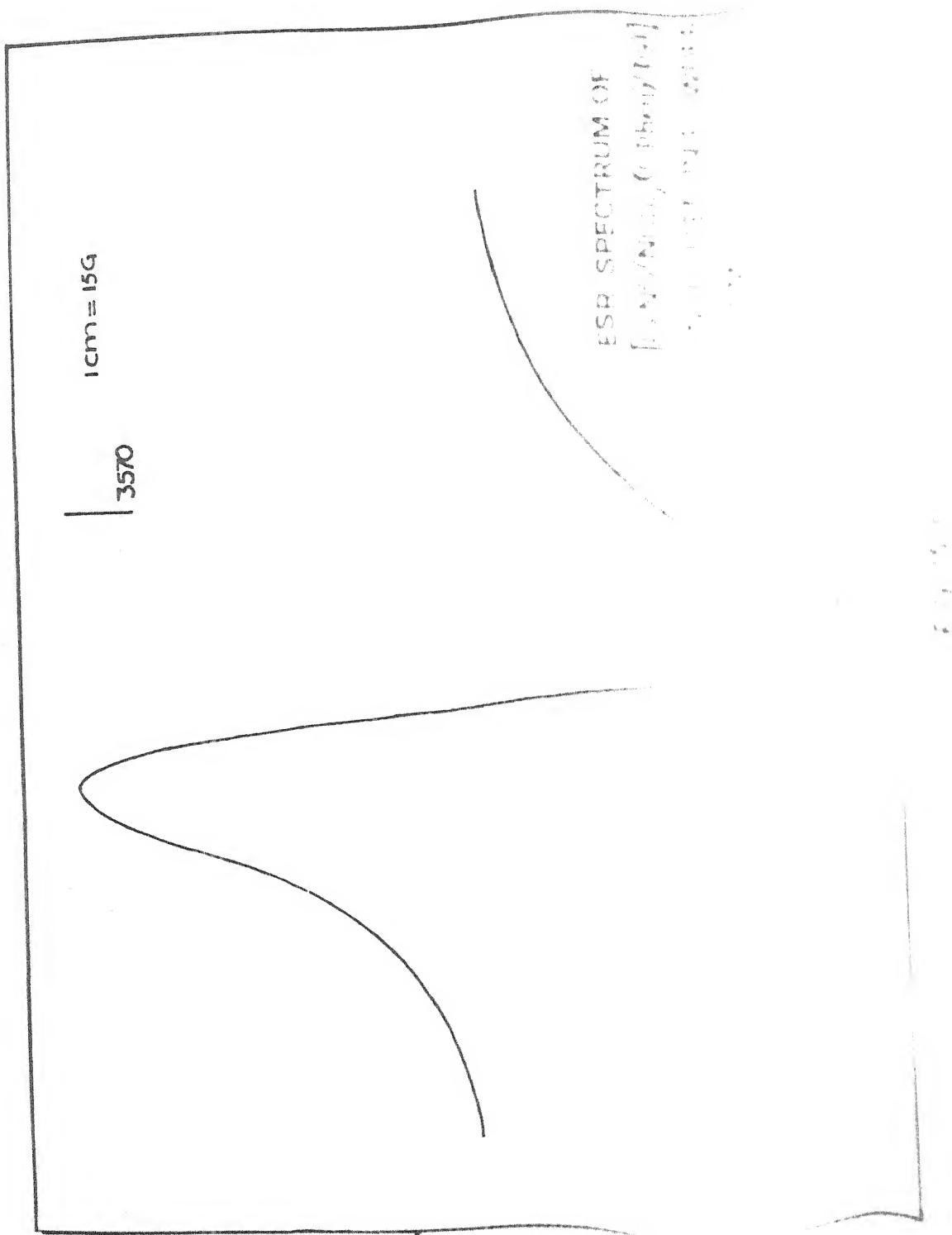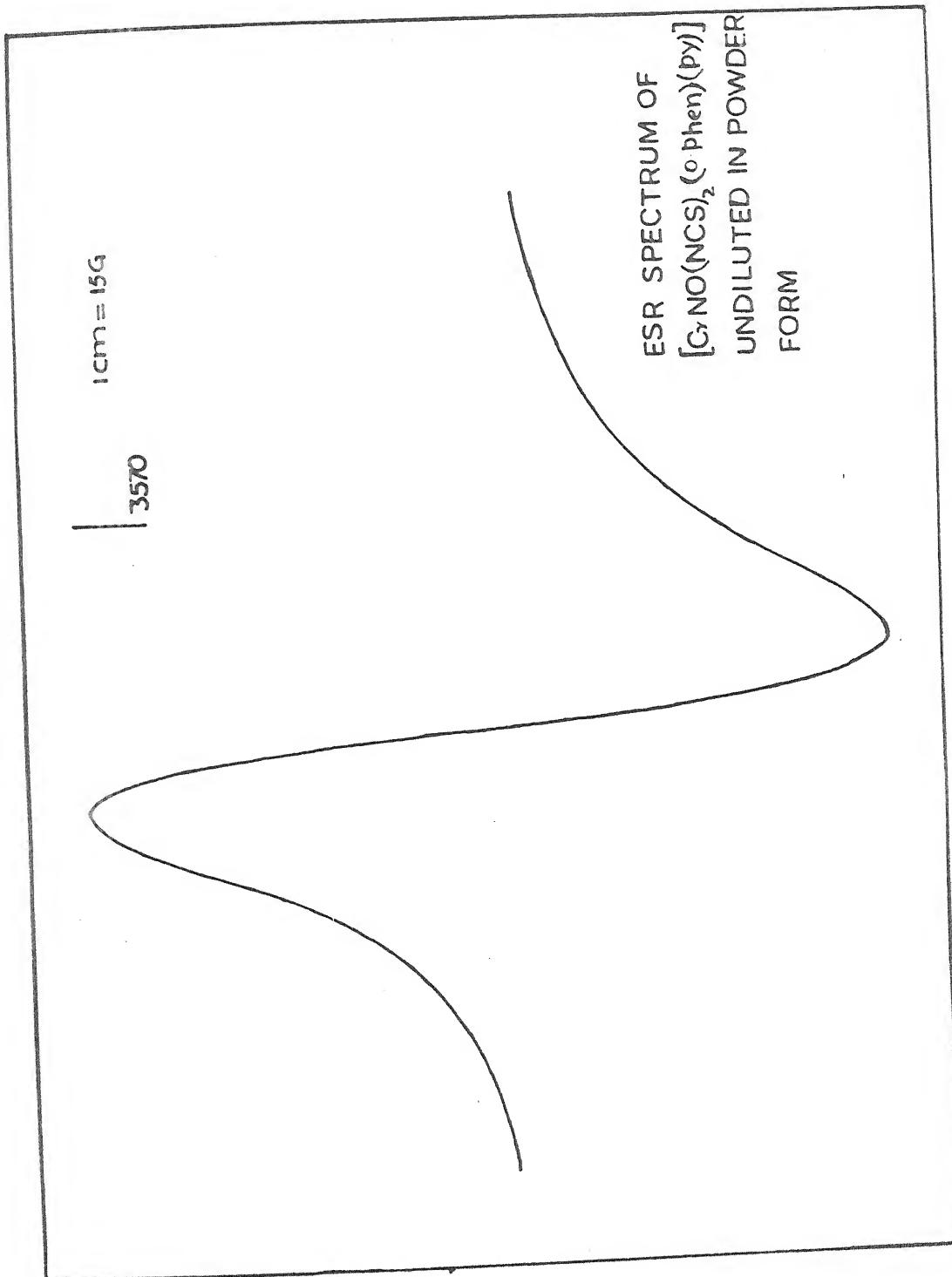
FIG·15(b)

in the complex. The value of g(ag) obtained from g
and g is in very good agreement with the 'g' value
obtained from undiluted spectra. A comparison of the
g(iso) and the nuclear splitting of the nitrogen,
A(n)of the complexes so far known suggest the delo-
calisation ability of the various ligands attached
to $(CrNO)^{2+}$ group as follows:

$$diars > CN^- > acac^- > NH_3 > SCN^- > H_2O .$$

However the 'g' value obtained from the solution
spectrum of acetylacetonato complex shows abit
higher value than that obtained fromthe solid spectra.
This suggests that in solution the complex may be
solvated in the axial position trans to NO. As
ethanol is used as a solvent the interaction with
the oxygen atom which has got no nuclear spin does
not produce any superhyperfine splitting (fig. 12b).
As a test a spectrum in ethanol treated with slight
pyridine is under taken. Fig. 12c shows that the
interaction of the pyridine's nitrogen (I=1) takes
place with the well resolved three lines spectrum of
the complex in ethanol. The ^{14}N nucleus of pyridine
interact causing a complex spectrum which would not
be resolved further. However, the 'g' value and the
complexity of the spectrum are suggestive enough to
say that the pyridine is coordinated at the sixth

site according to the following reaction.

$$[CrNO(acac)_2] + py \longrightarrow [CrNO(acac)_2(py)]$$

The corresponding dithiocarbamato complex as such has been isolated as hexacoordinated species. A comparison of the 'g' value (fig.14) with others suggests that its delocalisation ability falls in between cyanide and actylacetonate ligands.

The substituted cyanonitrosyl complexes are highly insoluble in nature and only the powdered spectra are taken which revealed nothing important to throw light for their lower magnetic moment values or about polymeric nature. However, a comparison of the cyano derivatives along with the thio-cyanato-derivatives resulted one interesting observation. The powdered spectra of $[CrNO(CN)_2(o\text{-phen})]$ and $[CrNO(NCS)_2(o\text{-phen})]$ presented in fig. 15a suggest that the line width (between point of maximum slope) of the cyano substituted complex is greater (93.0 gauss) than that of the thiocyanato substituted complex (42.0 gauss). Taking into consideration of the metal complexing ability of cyanide than thiocyanato group and the change in mass between these complexes by the units of two sulphur atoms, the broadening of the spectrum of the former complex may be attributed due to exchange broadening caused by interaction due

to polymeric state of the complex.

The ethanolic solution spectrum of $[CrNO(NCS)_2(o-phen)]$ (fig.13) consists of a broad line and the line shape shows the interaction of the super-hyperfine splitting due to ^{14}N of NO is masked by further hyperfine splitting from the ^{14}N nuclei of the two nitrogens of phenanthroline ligand along with those of the thiocyanate groups.

Mass spectra :-

The mass spectrum of $[CrNO(acac)_2]$ is presented in fig.16. Besides the appearance of parent ion peak at 280(M/e), ions like NO^+, Cr^+, $CrNO(acac)^+$, $Cr(acac)_2^+$ and $Cr(acac)_3^+$ are observed. The observation of each peak are in accordance with the different oxidation states of chromium. The most intense peak is observed for $Cr(acac)_2^+$. However, the molecular ion peak is of low intensity which is comparable to that observed in even for $Cr(acac)_3$[134]. However, the monomeric nature of the complex is here established.

X-ray photoelectron spectroscopy :-

The Xps spectrum of $[CrNO(acac)_2]$ in the binding energy range 395-415 eV is presented in fig. 17. The N(1s) value 401.8 eV is comparable to that reported for the $K_3[CrNO(CN)_5]$[55]. The slight increase may be accounted for the neutral nature of the complex

MASS SPECTRUM OF $\left[\text{CrNO(acac)}_2\right]$

FIG. 16
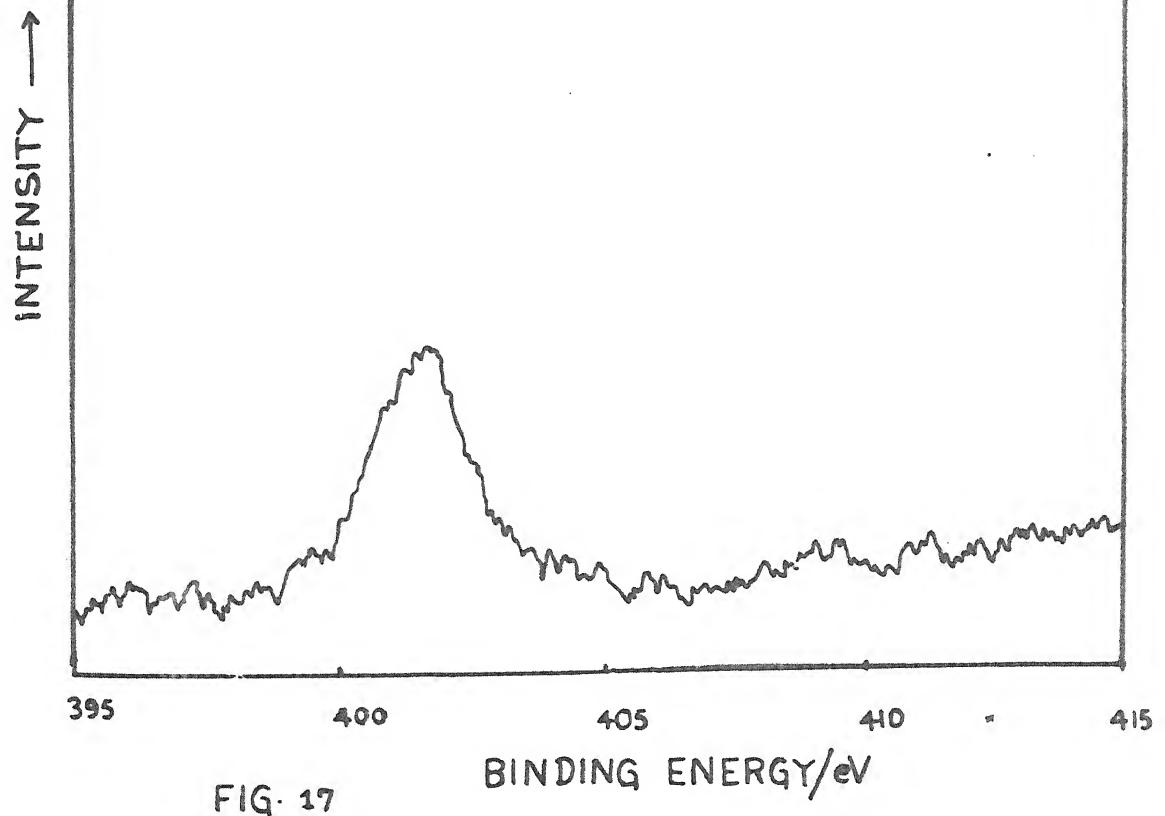
FIG· 17

compared to parent cyanonitrosylchromium(I)anion. The
slight increase of this value also tallies with the
increase of (NO) in its infrared spectrum (vide Supra).
The observed axial symmetry of the 'g' tensor for this
complex as discussed earlier is also in accord to the
presence of linear Cr-N-O Group.

Electronic Spectra :-

Reflectance spectra of the powdered solid com-
plexes, $[CrNO(CN)_2L_2]$ dipy, o-phen, 2 Qu, 2py) and
$[CrNO(acac)_2]$ and solution spectrum of the acetylacetonato
complex are recorded in the range 200-750 nm. Peak posi-
tions are presented in Table-20, where for comparison,
peak positions of the parent compound and of some alike
compounds as taken by Griffith[23] are also included. The
important feature of these electronic spectra is that
these complexes show four well resolved peaks, which
are numbered for convenience of reference as in Table-20.
The 3rd peak deserves special comments. For the isolated
complexes in this investigation, it is the most intense
peak among all the four peaks observed. The discussion
would be restricted here on dipyridyl substituted complex
taking it as representative of this class of compound
along with the acetylacetonato complex. For free dipy-
ridyl the first peak which appears at 280.1 nm., corres-
ponds essentially to $\pi - \pi^*$ transition. Coordination of

Table-20.

Electronic spectra*

Compound	1st	2nd	3rd	4th	Ref.
[CrNO(CN)₂(dipy)]	595.2	450.0	325.2	244.9	
[CrNO(CN)₂(o-phen)]	591.0	450.0	325.7	246.1	
[CrNO(CN)₂(Qu)₂]	632.9	449.6	327.8	248.7	
[CrNO(CN)₂(py)₂]	598.0	450.0	327.3	252.8	
[CrNO(acac)₂]	550.0	394.0	337.4	261.9	
[CrNO(acac)₂] in Methanol	550.0(32)	394.0(135)	337.2(3120)	270.0(1860) 254.9(1900)	
K₃[CrNO(CN)₅] in aqueous solution.	724.0(14.5)	447.0(127)	345.0(86)	270.0(2448)	23a
[CrNO(H₂O)₅](ClO₄)₂ in aqueous solution.	567.0(30.6)	447.0(131)	390.0(96)	324.0(101)	23a
[CrNO(NH₃)₅]Cl₂ in aqueous solution.	457.0(101)	348.0(69)	302.0(157)	257.0(1460)	23a

* Peak positions in nm and for solution spectra, extinction coefficients, (/mole^{-1}cm^{-1})in parentheses. Data taken from figs.18,19 and published results.

ELECTRONIC SPECTRUM OF $[CrNO(acac)_2]$
IN METHANOL

$2\times10^{-4}M$

$5\times10^{-4}M$

FIG. 18

ELECTRONIC SPECTRUM OF [CrNO(acac)₂] IN METHANOL

FIG. 18

REFLECTANCE SPECTRA

(-x-x-x-x-) [CrNO(CN)₂(o-phen)]
(-------) [CrNO(CN)₂(dipy)]
(-·-·-·→) [CrNO(CN)₂(py)₂]
(———) [CrNO(CN)₂(qu)₂]

nm

ARBITRARY O.D. ⟵
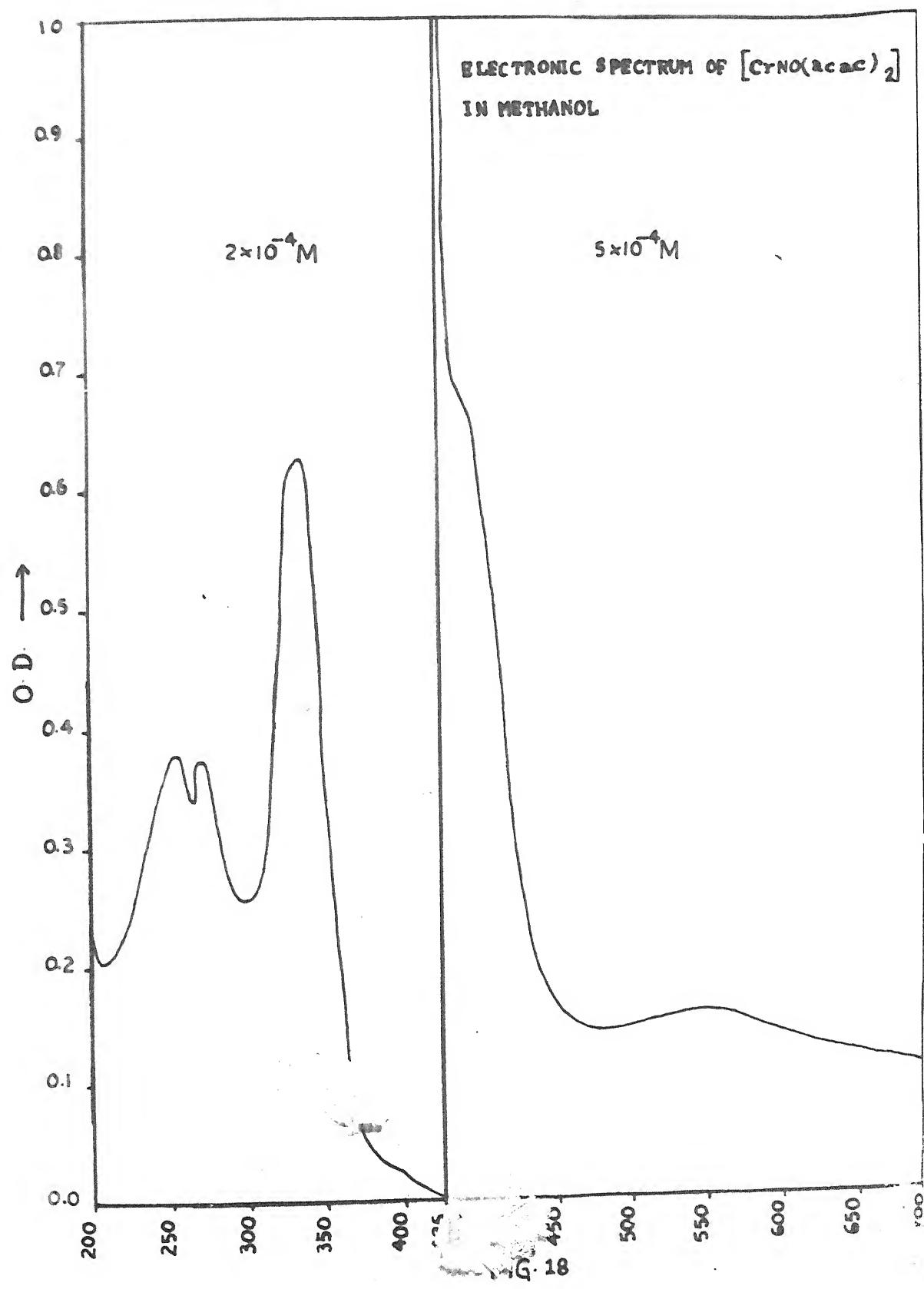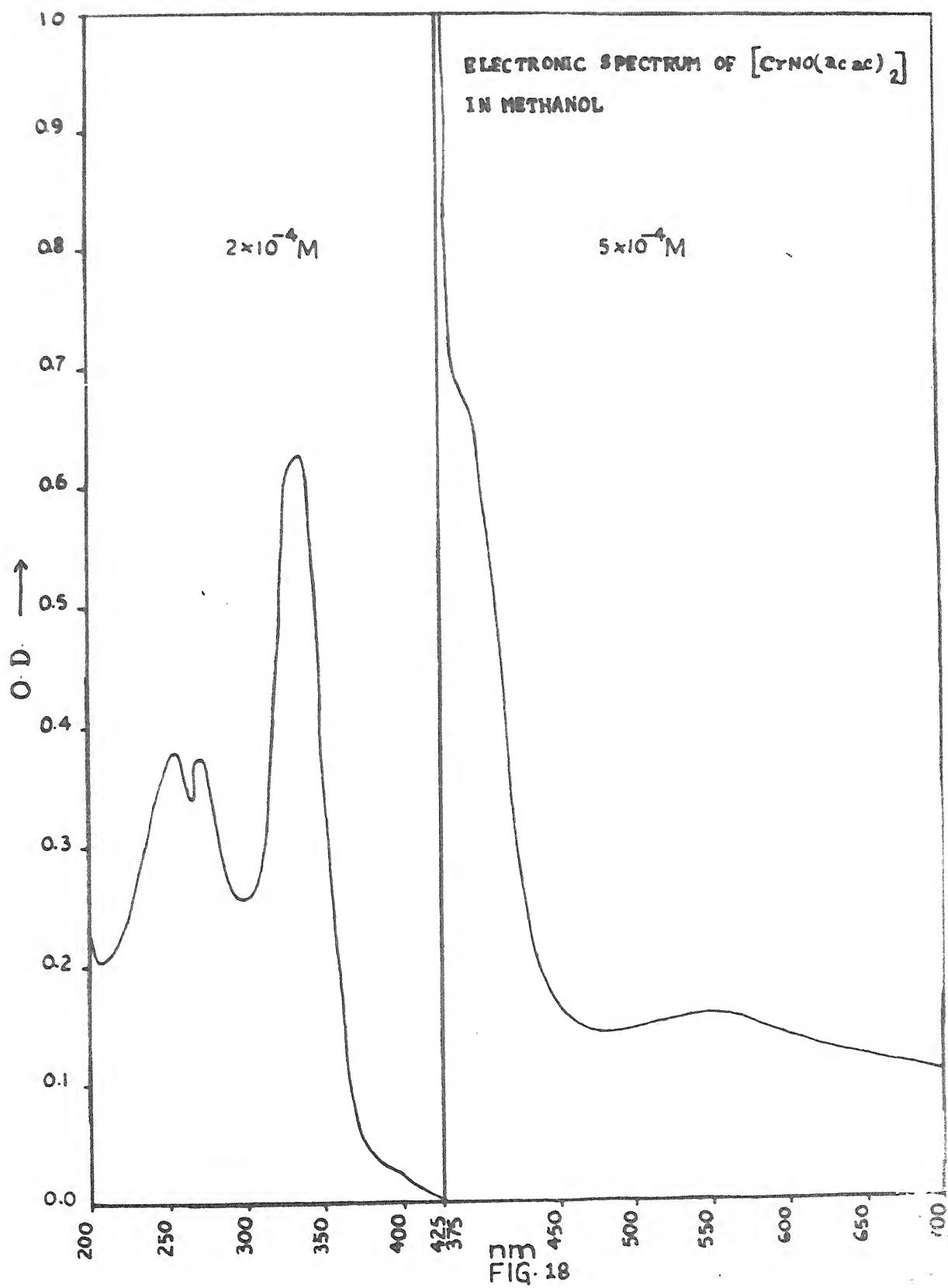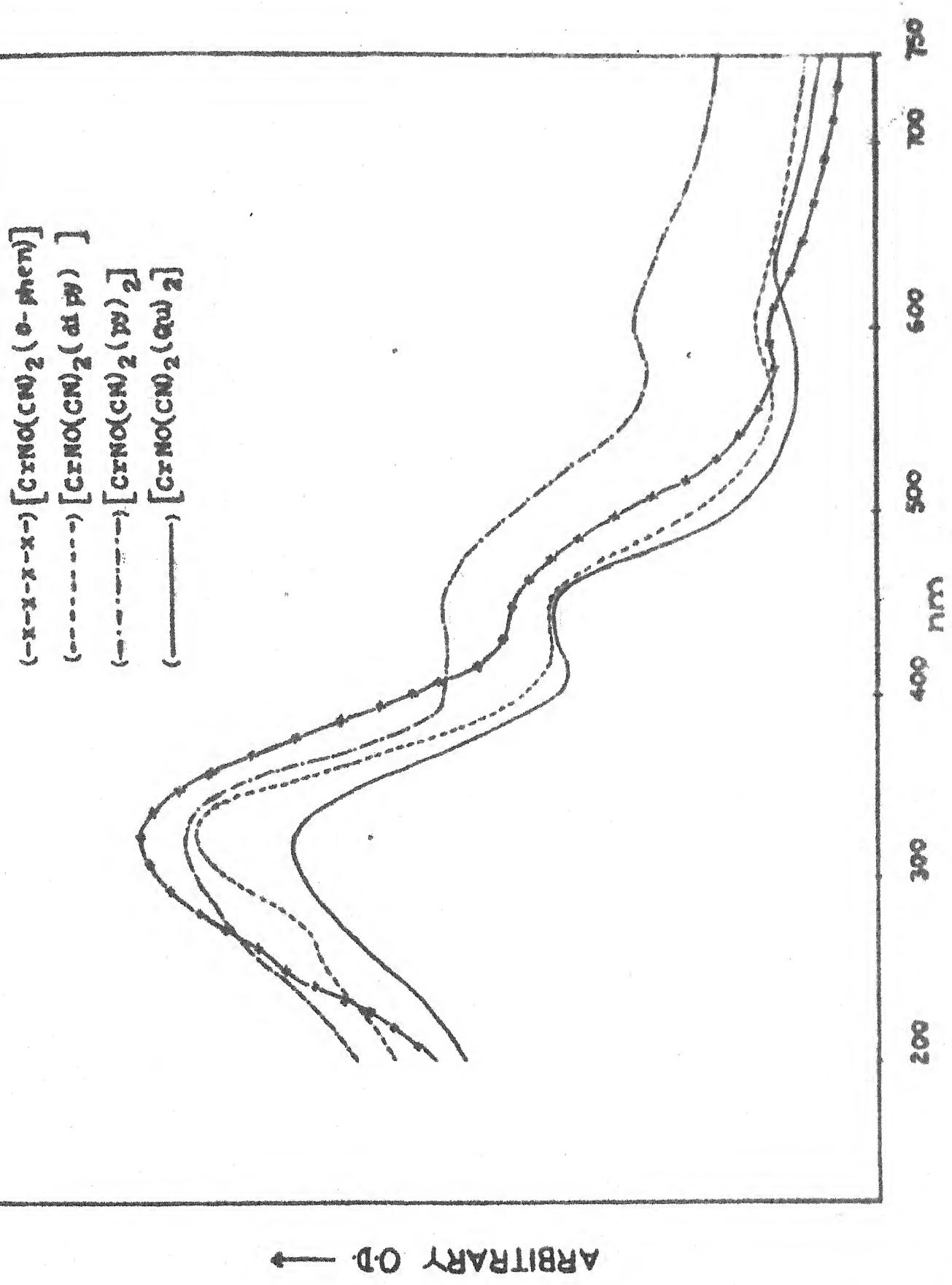
this with metal ion results in a red shift with the often splitting of this peak[135]. In identical nitrosylcyano complex of iron(II)[136] this red shift followed by splitting is clearly observed and the position of the appearance of this peak suggests that the π- system of the dipyridyl does not affect much the π-system of NO by comparing the peak positions of nitroprusside anion[43,137] with that of the dipyridyl substituted cyanonitrosyl of iron(II)[136]. The 3rd peak observed at 335.0 nm in pentacyanonitrosyl-chromate(I)anion is less intense than the 2nd peak, obviously it can not mask the $\pi-\pi^*$ transition of coordinated dipyridyl. Thus the 3rd peak at 325.2 nm is mainly responsible for $\pi-\pi^*$ transition of complexed dipyridyl. The appreciable red shift of this band which has no parallel in other dipyridyl complexes,[135,136] suggests the considerable mixing between the π- systems of dipyridyl and (CrNO)moiety in these complexes. The acetylacetonato complex also gives evidence of the considerable red shift of its $\pi-\pi^*$ transition that is from 290.8 nm[138] to 337.2 nm which also supports this view. From the intensity of the 4th peak in all these complexes along with the nature of the extinction coefficient of the acetylacetonato complex, it may be presumed that this peak for all these complexes can also be assigned to strong $\pi-\pi^*$ transition of the complexed ligand moiety[139,140]

For peaks Ist and 2nd, the low intensity nature of these peaks in all these complexes followed by extinction coefficients of such peaks of acetylacetonato complex suggest them predominatly of 'd-d' type transitions.

Unlike the e.s.r. spectrum (vide supra), the solution (methanol) electronic spectrum of bis (acetylacetonato) nitrosylchromium(I) does not give any clue of the solvation at the sixth position trans to NO as the solid state and solution electronic spectra of this compound give absorption peaks at indentical postitons.

Chapter IV

SUMMARY.

The thesis comprising the results of the investigations on the nitrosyl complexes of monovalent chromium, has been divided into three chapters.

In chapter I, a brief and general account of the cyanonitrosyl complexes has been given. The use of different physico-chemical methods in elucidating the bonding nature and structural aspects of these complexes are also reviewed. Based on these, a broad account of the chemistry of nitrosyl chromium(I) complexes has been given. From the synthetic point of view , the derivatives, the knowledge about which are only exist in solution studies,are synthesized. As an outcome of these, the scope of the present work has been stressed.

Chapter II describes the materials and methods involved in the present work in details which has been subdivided into two main parts. Chapter II- A describes the analytical methods used for the characterisation of the newly prepared complexes. Chapter II-B describes the preparation and properties of the newly synthesized compounds. As this type of substitution reactions have got no parallel among other nitrosyl cyano complexes of transition metals except ruthenium and to some extent iron, some analogies were tried to establish. Based on the substituent groups of these mixed ligand nitrosyl

cyano complexes of chromium(I), chapter II-B was further divided into four sub-headings. Chapter II-B.1 describes the preparation and properties of a series of nitrosyl chromium complexes having general formula $[CrNO(CN)_2L_2]$ (where L_2=o-phen, dipy, 2 Qu, 2 py, 2 picoline)starting from the substitution reaction of $K_3[CrNO(CN)_5].H_2O$ with these nitrogen donors. The reaction can be generalised as below.

$$K_3[CrNO(CN)_5]+L_2 \xrightarrow{dil.CH_3COOH} [CrNO(CN)_2L_2] + 3 CH_3COOK$$
$$+ HCN.$$
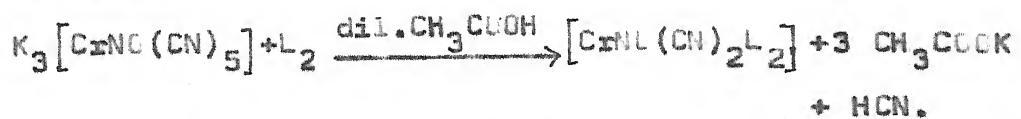
The remarkable chemical dissimilarties of these complexes with those of other metals nitrosylcyano derivatives were shown by comparison. Chemical inertness of cyano groups present in the representative complex, $[CrNO(CN)_2(dipy)]$ of this class has been shown by failure of the reaction of the following types :-

$[CrNO(CN)_2(dipy)]$ + excess dipy $\xrightarrow[\Delta]{sealed\ tube}$ no change.

$[CrNO(CN)_2(dipy)]$ + CH_3I $\xrightarrow[\Delta]{sealed\ tube}$ no change.

$[CrNO(CN)_2(dipy)]$ + CH_3I+HgI_2 $\xrightarrow[\Delta]{sealed\ tube}$ partial decomposition with no change.
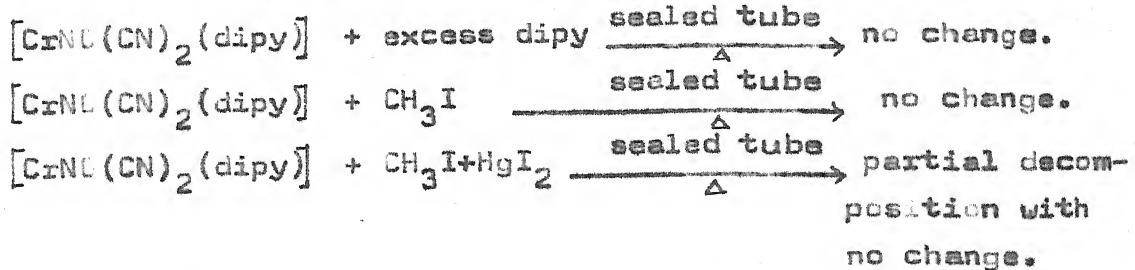
Chapter II-B.2 and B.3 describe the preparation and properties of bis(acetylacetonato)nitrosylchromium(I), $[CrNO(acac)_2]$ and aquobis (diethyldithiocarbamato)nitrosylchromium(I), $[CrNO(DTC)_2(H_2O)]$. Interestingly the corresponding dithiocarbamato complex can be isolated as

hexacoordinated species whereas the corresponding acetyla-
cetonato complex is pentacoordinated. In solution the
acetylacetonato complex remains solvated as $[CrNO(acac)_2S]$
(where S = donor solvent molecule). This has been particu-
larly demonstrated in ethanol solution using traces of
pyridine and the enteraction has been followed spectros-
copically (vide supra).

Chapter II-B.4 discribes the preparation and pro-
perties of the thiocyanato substituted complexes of the
general formulas $[CrNO(NCS)_2L_2]$ (L_2= dipy and o-phen) and
$[CrNO(NCS)_2L_2(py)]$. All these complexes are found to be
nonelectrolytic in nature.

Chapter III describes the physicochemical investi-
gations of the isolated complexes. The studies include
magnetic susceptibility, infrared, electron spin resonance,
mass, X-ray photoelectron and electronic spectral measure-
ments.

The magnetic moment values of the prepared complexes
after correction for diamagnetic contributions of the liga-
nds are in the range from 1.60 B.M. to 1.74 B.M. These
values are consistent with a low spin d^5 configuration.
This is in expectation as the ligands involved in the
preparation of the complexes are mostly π- bonding type
and hence should be of low spin type containing one
unpaired electron. The slightly higher magnetic moment

(1.87 B.M.) for the parent complex,$K_3\left[CrNO(CN)_5\right].H_2O$ is
due to spin and orbital interaction in the complex. It
is remarkable to note that the magnetic moment values
(1.60-1.66 B.M.) of the cyano substituted complexes are
lower than acetylacetonato complex. On the other hand
the magnetic moment values of thiocyanato nitrosyl
complexes are close to spin only formula. This suggests
the polymeric nature of the cyanonitrosyl complexes and
monomeric nature of the acetylacetonato and thiocyanato
derivatives.

Characteristic stretching frequencies of differ-
ent coordinating ligands have been assigned in the
infrared spectral studies. The $\gamma(NO)$ of the isolated
complexes is in the range 1694-1710 cm^{-1} which is com-
parable to the $\gamma(NO)$ of the known complexes. Solid
state spectra of all the cyanosubstituted complexes
give two cyanide stretchings in identical positions
that is at 2150-2156 and at 2125-2133 cm^{-1}. The lower
band appears as shoulder in all these complexes. The
$\gamma(CN)$ at 2150^{-56} cm^{-1} is assigned for the bridging cyano
groups and the rest one for each complexes for the
terminal cyano group. Various probable structures
have been assigned for these complexes. The structure,
fig.2c, is finally said to be correct among them. This
is in accordance with the investigation made by Bustin[118]

and valuable results of K. Nakamoto.[42]

The ν(NO) in aquobis(diethyldithiocarbamato)nitrosylchromium(I) is slightly higher than in acetylacetonato derivative and the dithiocarbamate is assigned as better complexing ligand than acetylacetonate.

In thiocyanato substituted complexes, the bonding of chromium through 'N' of the thiocyanato group is suggested by comparing the observed cyanide stretching in these complexes with those of the known thiocyanato complexes[42]. These complexes are assigned to be monomeric in nature due to lack of chromium to coordinate through 'S' of the thiocyanato group.

The ν(CrNC) and δ(Cr-N-C) have been assigned in the range 600-625 cm^{-1} and 595-600 cm^{-1} respectively for all the prepared complexes in this investigation.

Electron spin resonance spectral studies have been made for some of the prepared complexes. Tetragonal distortion in all these complexes is clearly reflected through the shape of the spectrum. The solvation in bis(acetylacetonato)nitrosylchromium(I) at the sixth position trans to NO is suggested through this study. The e.s.r. spectrum of this complex in ethanol treated with traces of pyridine shows the interaction of the pyridine's nitrogen(I = 1) with the well resolved three lines spectrum of the complex. The 'g' value and the complexity of the spectrum suggest that the pyridine is coordinated at the sixth

position. The 'g' value of the corresponding dithiocarba-
mato complex is compared with other complexes which indi-
cates that the delocalisation ability of this ligand is
in between cyanide and acetylacetonate ligand.

The e.s.r. spectra of the undiluted powdered
samples of $[CrNO(CN)_2(o-phen)]$ and $[CrNO(NCS)_2(o-phen)]$
clearly indicate that the line width of the cyanosubsti-
tuted complexes is greater than that of the thiocyanato
substituted complex. This broadening of the spectrum of
cyanosubstituted complexes may be presumed due to exch-
ange broadening caused by interaction due to polymeric nature
of the complex.

The only well established compound $[CrNO(acac)_2]$
containing oxygen as donor atoms of other co-ligands
has sharp melting point and hence subjected to mass
spectral studies. The observation of each peak in this
spectrum are in accordance with the different oxidation
states of chromium. The monomeric nature of the complex
is suggested through this study.

The X-ray photoelectron spectral studies is only
made for bis(acetylacetonato)nitrosylchromium(I) complex
due to the reason mentioned in above para. Other complexes
contain nitrogen donor which may affect the N(1s) binding
energy of the NO group and hence could not be subjected
to this study. The N(1s) binding energy value 401.8 eV

for this complex is comparable to the parent complex,
$K_3 \left[CrNO(CN)_5 \right] H_2O$.

The reflectance spectra of some of the cyanosub-
stituted complexes, $\left[CrNO(CN)_2 L_2 \right]$ (L_2= o-phen, dipy, 2py,
2Qu) and electronic spectrum of bis(acetylacetonato)nitro-
sylchromium(I) in methanol are described. All these
complexes show four well resolved peaks which are
comparable to those reported for the parent complex,
$K_3 \left[CrNO(CN)_5 \right] H_2O$.

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